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Tandem Strategy and Conversion Mechanism in Electrochemical CO₂ Reduction Reaction

By

Chubai Chen

A dissertation submitted in partial satisfaction of the
requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Peidong Yang, Chair
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Spring 2022

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Abstract

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Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Peidong Yang, Chair

Electrochemistry builds the bridge between renewable electricity and matter. As a promising branch of green chemistry, electrochemistry allows the transformation and utilization of carbon dioxide (CO₂) under mild operating conditions per the needs of carbon capture utilization and storage (CCUS). Interestingly, with the increase in electron numbers in the electrochemical CO₂ reduction, multiple products such as carbon monoxide (2e⁻), methanol (6e⁻), methane (8e⁻), ethylene (12e⁻), ethanol(12e⁻), and propanol(18e⁻) can be generated. As a double-edged sword, the broad spectrum of CO₂ electroreduction products ensures a large market size of downstream products but also puts forward great challenges for the electrocatalytic theory and process of CO₂ reduction. Catalysts play an instrumental role in activating the surface adsorbed molecules and modulating the pathway for molecular transformation, which determines the reaction kinetics, and catalyst selectivity, and therefore is regarded as one of the core components in the CO₂ electrolyzer. Suitable electrocatalysts, such as Au, Ag, and Cu, were found to be necessary to overcome the chemical inertness of CO₂ and minimize overpotentials. Specifically, Au and Ag are promising catalyst candidates for carbon monoxide (CO) generation while Cu is suitable to catalyze the carbon-carbon (C-C) coupling and generate multicarbon products in CO₂ electroreduction. Understanding and designing active catalytic sites for efficient conversion of CO₂ to multicarbons products (C₂+) through effective catalytic theory is of importance to the community.

This dissertation is to present a systematic study of rational design strategy in CO₂ electroreduction. In particular, it focuses on how the tandem strategy can facilitate practical CO₂ electrolysis. Within this scope, the methodology, universality of the tandem

strategy, structure and phase property of the bimetallic catalysts, and corresponding CO₂ transformation mechanism are discussed in detail.

Chapter 1 provides an overview of the CO₂ electrolysis. It introduces the background, utilization method, and the current progress and remaining challenges of the CO₂ reduction reaction with an emphasis on the corresponding catalyst design strategies. Moreover, the extension of CO₂RR from benchtop to industrialization is also briefly discussed. Chapter 2 demonstrates the feasibility and universality of tandem strategy in CO₂RR under industrial relevant current densities with Cu-Ag bimetallic catalyst on a gas diffusion electrode (GDE). The significant enhancement of multicarbon production rates can be attributed to the efficient Cu-Ag tandem strategy. Meanwhile, the increased intrinsic activity suggests the existence of new mechanisms in a CO-enriched local environment enabled by the tandem strategy. As the combination of Cu and Ag has been proved to be a good tandem CO₂RR electrocatalyst, chapter 3 focuses on the interaction and structural evolution of Cu-Ag nano-alloy under electrochemical CO₂RR conditions. It was found that Cu would gradually leach out from nano-alloy during electrolysis, leading to a phase separation process and the formation of thermodynamically stable inter-doped Cu- and Ag-rich grains. Further electrochemical Pb-UPD and *Operando* high-energy-resolution X-ray absorption spectroscopy (XAS) methods were utilized to reveal the surface property and dynamic evolution of Cu-Ag nano-alloy during CO₂RR. On the other hand, chapter 4 switches the focus from the exploration of tandem catalysts to the understanding of molecular transformation pathways in the tandem system. Inspired by the Wood-Ljungdahl pathway in natural CO₂ fixation, the asymmetric coupling process in CO₂RR was experimentally validated in aqueous CO₂ electrolysis by conducting isotope-labeled co-reduction experiments on the Cu surface where ¹³CH₃I and ¹²CO were co-fed externally as the methyl and the carbonyl sources, respectively. Cu-Ag nanoparticle assembly was further employed as a practical system to achieve asymmetric C-C coupling for CO₂ electroreduction. Chapter 5 closes this dissertation by summarizing the overall Ph.D. research and provides an outlook for the future research direction on electrochemical CO₂RR.

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*Dedicated to all those who experienced hardness today but tenderly look forward to a
better tomorrow*

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Chapter 1 An overview of Electrochemical Carbon dioxide Reduction Reaction (CO₂RR)

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1.1 CO₂ utilization in a carbon-neutral perspective

1.1.1 Trend and influence of global CO₂ emission

Carbon dioxide (CO₂), as the name suggests, is one of the final oxidation products of carbonaceous materials. Since the industrial revolution, fossil energy, including oil, coal, and natural gas, has been extensively used and regarded as the most important engine of economic development. Before green energy can be a mature alternative, to a certain extent, the consumption of fossil energy and the corresponding emission of CO₂ is even considered to be an important indicator of industrial production and economic prosperity. As an example, the United States contributed 25% of global historical CO₂ emissions ranging from 1751 to 2017, way higher than any other independent economy all over the world¹.

Unavoidable, the global emission of fossil-based CO₂ growth exponentially in the last century (Fig. 1.1a), making the concentration of CO₂ in the atmosphere far exceeds normal historical volatility (Fig. 1.1b)¹.

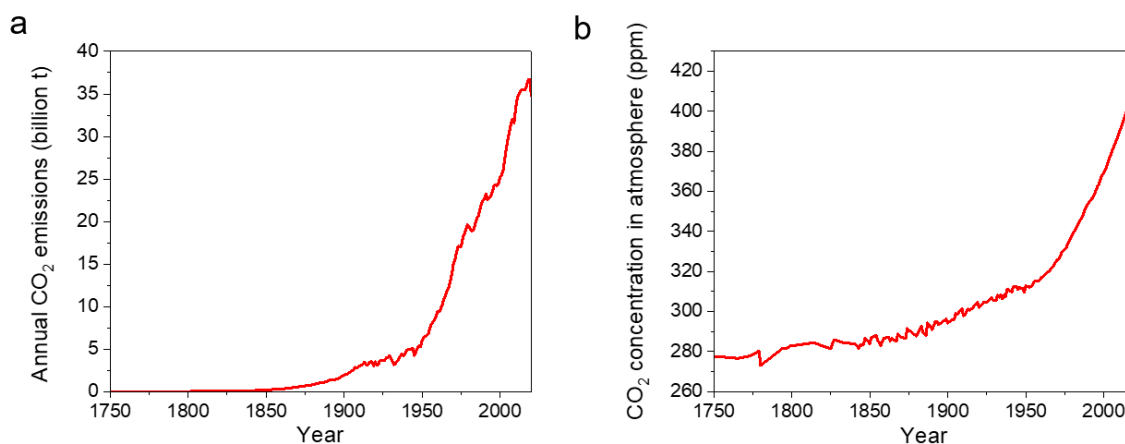


Figure 1.1. Historical data of the worldwide CO₂ (a) annual emission and (b) concentration in the atmosphere. Reproduced with open access permission from ref.1.

As a well-known greenhouse gas, the rapid increase in the concentration of CO₂ in the atmosphere has put enormous pressure on the global climate system. Although there is a sound that the significant climate change in the past few decades is a natural manifestation of the cycle of cold and heat in nature but not the effects of greenhouse gases, it must be recognized that for the environment on earth, which is an extremely complicated nonlinear system, the impact of CO₂ concentration increase is huge and multi-dimensional.

Global warming already causes droughts in some areas but floods in others due to enhanced evaporation and disturbance of the atmospheric circulation system². Not to mention the potential humanitarian threat posed by rising sea levels to Pacific Island nations. The increased frequency of extreme climates in the past decades indicates that the carrying capacity of the environment is approaching its limit.

On the other hand, as the acidic gas, CO₂ also influences the pH value of the water system. As a direct result, the acidified water can be more corrosive to the shells and coral reefs due to the reaction with CaCO₃. Meanwhile, the population of microbes may also vary due to the change in the environment³.

Although it is widely recognized that curbing excessive CO₂ emissions is a huge global environmental governance problem, unfortunately, like a prisoner's dilemma, individual economies lack sufficient motivation to pay the price due to the strong correlation between social prosperity and energy security. Thus, the signing of the Paris Climate Agreement in 2015 gave the world a shot in the arm. Under the framework of the Paris Agreement, 195 countries around the world have unioned together, using a systematic effort to limit the rise in average global temperatures to less than 2 °C above pre-industrial levels. However, standing in 2022, the implementation of the Paris Climate Agreement by all countries in the world has not been as smooth as expected. The arbitrary withdrawal and re-entry of the United States for political reasons has further cast a shadow over the prospects of the Paris Agreement.

There is a growing realization that reducing CO₂ emissions at the expense of unduly inhibiting economic development is not practical. Therefore, the consensus on the necessity of energy structure adjustment has gradually spread from professionals to all walks of life. Just like the changes and opportunities brought by the Internet, the rise of renewable energy will bring another revolution.

1.1.2 The rise of CO₂ utilization

According to its chemical and physical properties, CO₂ has a wide range of applications in the food industry (such as soda and beer production, alcohol fermentation), agriculture (such as gas fertilizer in the greenhouse), daily life (such as fire extinguishers, dry ice fogging), *etc.* Nevertheless, among these applications, most of the CO₂ is eventually released into the atmosphere at the final. This fact indicates that these utilization methods indeed do not have the potential to solve the CO₂ emission problem.

Fundamentally, to reduce the concentration of CO₂ in the atmosphere, CO₂ is supposed to be chemically or physically fixed into some permeant or at least semi-permanent stable states.

Similar to filling CO₂ into a soda bottle, one of the emerging carbon storage techniques is to fix CO₂ into the deep saline aquifers⁴. The temperature and pressure there are sufficient to transform CO₂ into a supercritical state and be sequestered accordingly. However, there is no predictable profitability in this process, and it is difficult to reversibly reuse this part of the carbon dioxide. Although the global saline aquifers have an amazing carbon dioxide storage capacity, this technical route is still facing a huge challenge to be widely adopted.

On the same track, the possibility to seal CO₂ into an oil well is also under development in order to fix CO₂ and improve the crude oil yield at the same time. This CO₂ enhanced oil recovery technique (CO₂-EOR) technique route is favored due to its scalability and profitability. Although there are some pilot projects in various countries⁵⁻⁶, the future unit cost of obtaining CO₂ largely determines the development prospects of these projects.

More ambitious technological pathways aim to convert carbon dioxide directly into valuable chemicals. Due to the transformation process on the molecular level, the transformation of carbon dioxide is theoretically permanent. Since this transformation involves the break of inert C-O bond in CO₂, sufficient energy input and efficient catalyst are required to overcome the activation energy barrier. Varied energy sources, such as thermal energy, electricity, light, and their combinations are utilized to achieve this goal⁷⁻⁹.

Although various new catalytic technologies are attractive, thermo-catalytic processes are still the absolute mainstream in the traditional chemical industry. The transformation of CO₂ in thermal catalysis is through the reverse water gas shift (RWGS) reaction¹⁰, in which carbon dioxide can react with hydrogen (H₂) to produce carbon monoxide (CO) and water (H₂O) vapor (equation 1.1). Meanwhile, H₂ in the industry mainly comes from the steam reforming process of methane (equation 1.2). Naturally, through the rational design of the catalytic process, the dual reforming technology of carbon dioxide and methane can be realized in tandem with these two catalytic processes, thereby producing syngas that is widely used in industry (equation 1.3). Researchers also intend to further upgrade the final products to multicarbon alkanes¹¹, aromatics¹², alcohols¹³, *etc.*



Thermodynamically, the occurrence of the reaction requires the Gibbs free energy change of less than 0, which can be achieved by tuning the reaction temperature. However, an alternative choice is to change the applied voltage in the electrochemical cell. Compared with the high-temperature requirement in thermal catalysis, electrocatalysis only needs an applied potential within a few volts, which greatly reduces the requirements for the

reactor. Therefore, electrocatalysis has been regarded as a very promising technology route to achieve CO₂ transformation. It has been found that multiple products can be produced by CO₂ electrolysis, including syngas, formate, methane, ethylene, ethanol, *etc.* The current research on CO₂ electrocatalysis mainly stays in the laboratory stage. There is still a lot of effort that is needed to develop stable catalysts with low catalytic overpotential and high selectivity. Meanwhile, the exploration of suitable electrolytic cell configurations to increase energy efficiency and mass efficiency is also important to the industrialization of electrochemical CO₂RR.

As the major global energy source, sunlight offers 3.85 YJ of energy to the earth annually¹⁴. There are great potentials to directly utilize this energy in CO₂ transformation by mimicking the natural photosynthesis process¹⁵. Although most of the CO₂ photocatalysis can only transform CO₂ into CO, recently there are also some efforts that try to produce deep reduced products, such as CH₃OH¹⁶, C₂H₄¹⁷, or C₂H₆¹⁸ from CO₂. Currently, the major problem of photocatalytic CO₂ transformation is the low quantum efficiency under AM1.5 spectrum and also the sluggish turnover frequency.

Besides the most popular thermal-, electro-, and photo- CO₂ transformation technical routes, there are also some other hybrid methods. For example, photothermal CO₂ transformation takes advantage of the hot electron excited from the photochemistry process but also accelerates the reaction rate by additional thermal energy input⁸. Similarly, photoelectrolysis technique can reduce the overpotential required in pure electrocatalysis, more efficiently achieve CO₂ transformation¹⁹, and even construct a bias-free electrochemical configuration²⁰. Even the magnetic field was also found can be utilized in CO₂ electroreduction to decrease the cell overpotentials²¹.

Although various strategies for CO₂ conversion are flourishing, the development of efficient, highly selective, and long-lived catalysts remains a central issue in CO₂ conversion.

1.2 Electrochemistry in CO₂ transformation

1.2.1 Basic concept of electrocatalysis

As a large category of chemical reactions, redox reactions play an important role in catalytic chemistry. Although redox processes can be very complex, their essence is simply the gain or loss of electrons. Interestingly, the generation of current is the directional movement of the carriers (electron, hole, or ions) under the potential difference. The directional flow of electrons can be exploited to drive redox reactions under suitable conditions (eg, electrical potential, catalytic materials, reactants, *etc.*).

The device that realizes this reaction process is called an electrolytic cell (or primary cell when output energy) (Figure 1.2). In contrast to the direct transfer of electrons between two molecules/ions in chemical redox processes, electrochemical redox processes use current as the mediator to split redox reactions into spatially separated oxidation and reduction reactions. The electrode where the oxidation half-reaction takes place is called the anode. Similarly, the reduction half-reaction takes place on the cathode. It is notable

that there is not an absolute value of the electrochemical potentials so a reference electrode was also inducted into the system to standardize the applied potential on the anode and the cathode. In the aqueous environment, ions, rather than electrons, are the charge carriers in the aqueous electrolyte. In the actual electrocatalytic process, the electrolyte also plays many important roles in addition to being the carrier. For example, buffering the pH near electrodes during catalysis, which is strongly correlated to the molecular transformation pathways, regulating electrocatalytic activity through cation and anion effects, *etc.* Ion exchange membrane is widely used in electrosynthesis to spatially separate anode and cathode, allowing the specific carriers to pass but block the others, therefore avoiding some unexpected side reactions.

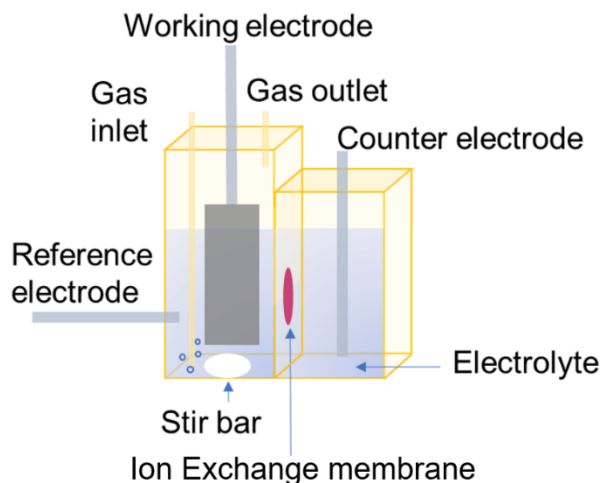


Figure 1.2. A schematic illustration of a typical two-chamber electrochemical cell with a three-electrode configuration.

An important descriptor in electrochemistry is the overpotential, which is used to quantify the extra potential needed compared with the thermodynamic potential in order to make the reaction happens. The overpotential is actually unavoidable due to the reaction's activation energy barrier, mass transport, and electrolyte resistance. One major target of the electrocatalyst development is to decrease the overpotential in the reaction by minimizing the activation energy barriers (Figure 1.3). Mass transport is more or less influenced by the morphology of the nanocatalysts, but more critically, it has been found that the rate of mass transport at the three-phase interface is orders of magnitude higher than that in the aqueous environment. More details about the mass transport and the application of gas diffusion electrodes in CO₂RR will be discussed in section 1.3.2. An important factor that is normally ignored in lab-scale electrolysis is the Joule heating induced by the passed current. The Joule heating not only decreases the full cell energy efficiency but also disrupts the steady operational condition of the reaction. Increasing the electrolyte concentration or optimizing the cell configuration can significantly ease Joule heat generated by the full cell resistance.

Electrocatalysis plays an important role in the interconversion of electrical and chemical energy. For example, hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) has been utilized for the fuel cells. Due to the difficulty of hydrogen storage, other fuels, such as methanol, and ethanol, are regarded as the alternative choices in the oxidation half-reaction. In the reverse way, electrocatalytic water splitting was used to generate high purity hydrogen and oxygen through hydrogen evolution (HER) and oxygen evolution (OER) half-reactions. Similarly, CO₂ can also be reduced on the cathode facilitated by the proper electrochemical catalysts. However, hydrogen evolution reduction is always the competing reaction with the CO₂RR in the aqueous environment. Therefore, solving the question that how to direct the proton or the surface absorbed H into the CO₂ transformation pathway rather than the hydrogen evolution requires the development of catalysts with high catalytic selectivity.

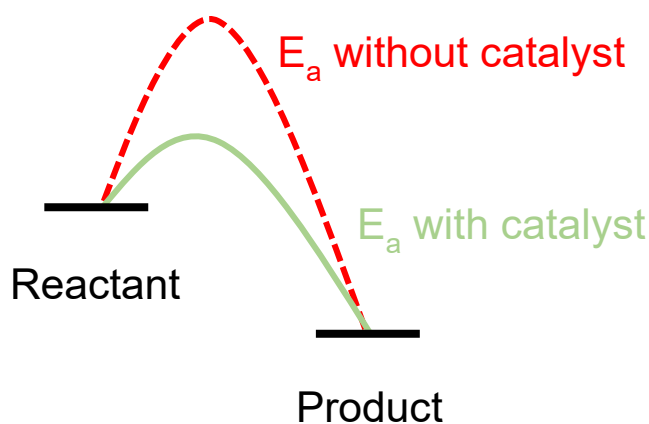


Figure 1.3. A schematic illustration of the activation energy barriers with and without a catalyst.

1.2.2 Electrochemical practice in CO₂ transformation

Compared with HER, ORR and other electrochemical reactions that can directly read the catalytic activity through current density and overpotential, it is much more complicated to study the CO₂RR. Therefore, as a necessary complement to the more general electrochemical research paradigm, this section briefly describes some of the additional precautions needed to study electrochemical CO₂RR processes.

Contaminations: A trace amount of the contaminations in the system may vary the catalytic selectivity of the CO₂RR²². However, researchers also use this phenomenon to tune the syngas ratio (H₂ and CO) in CO₂RR²³⁻²⁴. Using high purity chemicals and CO₂ gases can minimize the contamination influence in relatively long time electrolysis²⁵. Ion exchange resins, such as Chelex, can also be used to pretreat the chemicals and reduce the impurity of high valent ions.

On the other hand, contaminations can also stem from the electrodes. Since Ag/AgCl reference electrode is commonly used in CO₂RR, the leaking of the Ag⁺ ions from the reference electrode may influence the catalytic performance²⁶. A double junction reference electrode can mostly eliminate the leaking problem. Meanwhile, due to the oxidation reaction happening on the anode, the corrosion effects are also possible to induct contaminations. Based on previous research on the HER, people found that the Pt can leach out during the electrolysis and then diffuse to the cathode, which may enhance the HER selectivity. Nevertheless, potential organic contamination might be induced if the carbon rod is used as the anode²⁷. Since the organic contamination can significantly influence the liquid product analysis, as a compromise, Pt is still the most common counter electrode choice.

Products analysis: Multiple products can be generated in CO₂RR, which is especially true when Cu is used as the catalyst. Therefore, the current density under certain overpotentials is no longer a direct parameter to represent the catalytic performance of CO₂RR. Further products analysis is necessary. Typical gas products in CO₂RR, such as CO, C₂H₄, and H₂ can be easily quantified by gas chromatography (GC) with proper column configuration. However, the liquid product analysis is much more complicated. Currently, most of the published research uses nuclear magnetic resonance (NMR) to probe the liquid products with a solvent suppression method. Sometimes, high-performance liquid chromatography (HPLC), and headspace gas chromatography (HSGC) are also used to quantify the liquid products. But the detection limit of HPLC is higher than NMR and HSGC is not suitable for non-volatile products. So they are not as popular as NMR.

Aldehydes are the CO₂RR products that are difficult to be quantified. They go through reversible polymerization under basic conditions, thereby losing the NMR response. Therefore, neutralizing the electrolyte is necessary before the NMR test if buffer solution is not used as the electrolyte. Meanwhile, since aldehydes can be hydrated to form diols, the corresponding diol peaks should also be quantified and added together.

Conservation of matter: Theoretically, every electron utilized in the electrolysis can be found in the molecule of generated products. However, practically, the mass constant is not always satisfying. One possibility is that the side reaction happens. For example, when O₂ exists in the electrolyte, ORR rather than CO₂RR happens on the electrode and generates H₂O, which cannot be quantified. Meanwhile, the prepared electrocatalysts may also contain some oxidative species that can be reduced under the applied potential and therefore consume the input electrons. Another possibility is the inaccurate calibration curve, which underestimates or overestimates the exact yield of the products. Only if all the procedures are correct, the add-up faraday efficiency (FE) of multiple CO₂RR products can be close to 100%.

1.3 Challenge and Catalytic strategies in electrochemical CO₂RR

1.3.1 Challenges in electrochemical CO₂ transformation

So far there are still lots of challenges in the electrochemical CO₂ transformation that are waiting to be solved. Here, in order to sort out the main challenges in the CO₂ electroreduction logically, we briefly discuss how CO₂ molecules in the gas phase are transformed into the CO₂RR products.

As shown in Figure 1.2, CO₂ is continuously bubbled into the electrochemical cell and generates CO₂ saturated headspace. Based on Henry's law, the CO₂ solubility in the electrolyte is related to the partial pressure of CO₂ in the gas phase. Meanwhile, the balance between CO₂ and carbonic acid also influences the concentration of free carbon dioxide. Then, the CO₂ diffuses from the bulk electrolyte to the electrolyte-electrode interface, which we normally called the double layer, and is absorbed on the catalyst surface. Afterward, CO₂ is activated on the catalyst surface and goes through bond cleavage and formation to generate the targeted products.

Although the whole process is subtle and complicated, it can be simply separated into two main parts: CO₂ mass transport and CO₂ activation.

By optimizing the mass transport, CO₂ is supposed to maintain suitable concentration over the catalyst surface to ensure a sufficient mass supply. Meanwhile, developing better catalysts to activate CO₂ under lower overpotential and with higher catalytic selectivity is always one of the central questions in the CO₂RR community.

1.3.2 Mass transport in CO₂RR

Presently, three typical configurations of the electrochemical cell normally used by researchers are the H-cell, the flow cell with gas diffusion electrode (GDE) and the Membrane Electrode Assembly (MEA) (as shown in Figure 1.4). The most common cell on the benchtop is the H-cell, whose name stems from the cell configuration of two chambers and a bridge. The cathode is fully immersed in an aqueous electrolyte in an H-cell. Therefore, as described in section 1.3.1, CO₂ needs to firstly dissolve into water and then diffuse to the cathode surface, which process is limited by the solubility limit and the diffusion coefficient of CO₂ in water. So the aqueous CO₂ electrolysis in such cells is limited to tens of milliamps. Organic solvents, such as methanol or acetonitrile have much large solubility of CO₂ than water²⁸. However, the electrolysis of CO₂ in organic solvents can only generate oxalate, formate and carbon monoxide due to the insufficient proton source. Since hydrocarbons and multicarbon oxygenates cannot be generated, organic CO₂ electrolysis is out of the scope of this dissertation and is not detailed discussed here. In the aqueous system, some surface modification methods can make the surface more hydrophobic and enhance local CO₂ concentration by introducing some weak basic function groups²⁹⁻³¹. Notably, some surface modifications are also directly involved in the CO₂ activation, but this is discussed in the next section. Although surface modification can increase the local CO₂ concentration, it cannot bypass the limitation of CO₂ in the aqueous environment.

In contrast to the H-cell, the GDE configuration exposes one side of the cathode to the feeding gas, thus allowing the co-existence of the liquid phase and gas phase within the catalyst layer. Recently, emerging GDE works have rapidly broadened the scope of CO₂RR and pushed current densities to a more practical level³²⁻³³. This configuration not only dramatically mitigates the CO₂ mass transport limitation but also allows experiments to be conducted in highly alkaline electrolytes. The MEA configuration leverages the GDE configuration of a flow cell while minimizing electrolyte usage by direct contact of the catalyst layer with the ion exchange membrane. This configuration can mitigate the full cell resistance and improve cell stability.

In particular, a recent popular development in the electrocatalytic community has been to employ highly alkaline (e.g. 1M KOH or greater) electrolytes in a GDE environment to boost catalytic activity. CO₂RR selectivity is enhanced under high alkaline conditions due to the suppression of the hydrogen evolution reaction (HER). Furthermore, any elementary steps of CO₂RR that involve the H^{*} species (such as CH₄ production) will also be influenced³⁴. Multicarbon products like C₂H₄ or C₂H₅OH generally exhibit less local pH dependence since the rate-determining step (RDS) is the C-C coupling reaction³⁵. Interestingly, it has been found that under highly alkaline conditions (such as in >1 M KOH), OH⁻ ions play more diverse functions. OH⁻ influences Bader charge of catalyst surfaces³², tunes the catalytic pathway by nucleophilic reaction with surface intermediates³⁶, and may potentially influence the H-bond network, near-surface electric field, *etc.*

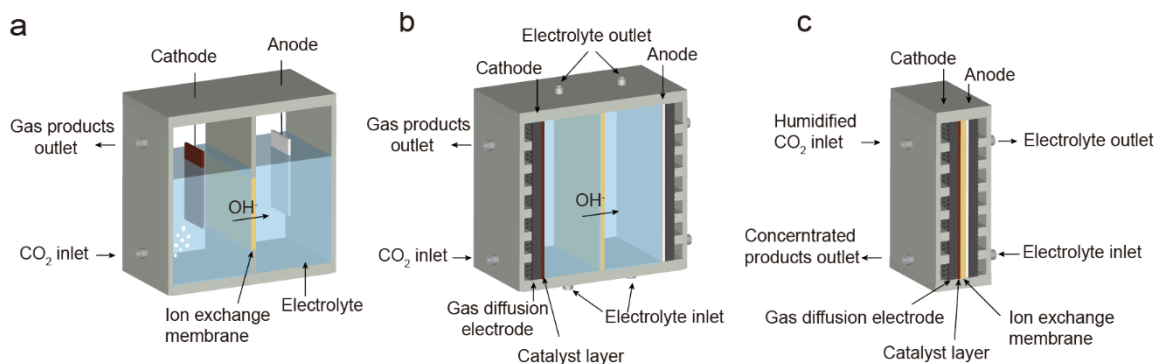


Figure 1.4. A schematic illustration of different electrolyzer configurations. (a) conventional H cell. (b) flow cell with a gas diffusion electrode. (c) membrane electrode assembly.

However, we emphasize that the utilization of alkaline electrolytes is not an ultimate solution for high efficient CO₂RR. The sustainability of this practice towards overall CO₂ reduction has recently been called to question³⁷. The disadvantage of using high alkaline electrolytes under real operating conditions is too significant to ignore. The unavoidable reaction between OH⁻ and CO₂ results in the formation of carbonate/bicarbonate and irreversible acidification of the electrolyte. The resulting carbonate generation can reduce

the accessible CO₂ feedstock for electrolysis, increase whole-cell resistance, block the gas diffusion channel, and accelerate electrolyte flooding, ultimately shutting down the cell. For comparison, although the locally generated OH⁻ at the cathode in neutral electrolytes can also react with CO₂, the generated carbonate/bicarbonate is overall balanced with the anodic half reaction, in which the carbonate/bicarbonate can react with generated protons and release CO₂ back to the gas phase. While this results in the net transfer of CO₂ from cathode to anode, this is a more tenable problem than the irreversible acidification of KOH. Furthermore, the consumption of the feeding gas and alkaline electrolyte increases economic costs and significantly suppresses the CO₂ concentration near the catalyst surface. As Rabinowitz, J. A. *et. al.* recently discussed, underestimating or ignoring energy consumption of recycling CO₂ and OH⁻ from CO₃²⁻ will lead to over-estimated CO₂RR energy efficiency and a misleading techno-economic model³⁷. Recent techno-economic models have begun to take this into account and evaluate the future of CO₂RR from technology to market³⁸; additional comprehensive analyses of CO₂ transformation considering CO₂ and electrolyte regeneration and barriers towards commercialization would be intriguing additions to the literature.

1.3.3 Catalyst design strategies in CO₂ activation

Over the past decade or so, a large number of catalysts have been developed for electrochemical CO₂RR and produce a variety of different reduction products. So the classification of the catalytic strategies seems to be complicated.

However, if thinking about the CO₂ activation process from a more essential point of view, knowledge developed in the previous surface chemistry community is still very helpful. As the Sabatier principle mentioned, the binding strength of the catalyst surface to the intermediate has a crucial impact on the catalytic performance. There are multiple intermediates in the carbon dioxide process which makes the application of the Sabatier principle a little harder here. The bonding strengths of different atoms to the catalyst surface, including C, H, and O, all have a significant effect on the catalytic process. Recently, a smart category method uses the metal-hydrogen (M-H) and metal-oxygen (M-O) binding strengths to separate catalysts in four different regions³⁹.

Qualitatively, within a certain range, stronger M-H binding strength can promote the occurrence of HER, thereby inhibiting the occurrence of CO₂RR. Pt is exactly a typical metal that has high M-H affinity but weak M-O affinity. On the other hand, the stronger M-O binding strength will promote the binding of the O atom of the CO₂ molecule to the catalyst surface. In this case, CO₂ cannot be further hydrodeoxygenated to generate CO intermediates but is converted to formic acid. Sn, Bi, and In are typical formate generation catalysts⁴⁰⁻⁴² with weak M-H affinity and high M-O affinity. Metals, such as Au⁴³⁻⁴⁴, Ag⁴⁵⁻⁴⁶, and Zn⁴⁷⁻⁴⁸ have a relatively weak binding affinity with both H and O, therefore are potential good catalyst candidates for CO₂ to CO transformation. Pd⁴⁹ also exhibits appreciable CO₂RR catalytic activity even though it has a relatively strong binding with H.

Cu, as a very special metal catalyst in CO₂RR, is the only metal that has proper binding strength to the intermediate and therefore can transform them into multicarbon products.

This special proper of C-C coupling highly depends on the surface structure of Cu as the formation of the Cu-Au intermetallic alloy cannot boost but lose the FE towards multicarbons⁵⁰.

Therefore, the study of Cu single crystal facets is regarded as an important fundamental research direction for Cu catalytic sites. By performing CO₂RR on the single crystal face and analyzing the products, researchers found that the (111) facet of Cu is relatively inert and has the lowest selectivity for multicarbon products. As a comparison, (100) and (110) have higher activity toward multicarbon products generation. High-index facets composed of (100) and (110) have the optimum catalytic selectivity⁵¹⁻⁵². The underlying mechanisms were further discovered with both CO reduction reaction (CORR)⁵³⁻⁵⁴ and density function theory (DFT) calculation⁵⁵⁻⁵⁸. These understating also guided the development of faceted nano-structured catalysts in practical CO₂ reduction⁵⁹⁻⁶⁴.

During the development of CO₂RR nanocatalysts, it was also found that catalysts with rough surfaces generally have better performance in CO₂RR. The electrochemical surface area (ECSA) of the Cu catalysts not only influences the current density but also directly influences the selectivity toward multicarbons. In fact, multiple different effects may collectively contribute to this observation. For example, localized nanostructures can prolong the retention time of intermediates⁶⁵. Meanwhile, the high current density generated by the rough surface will increase the local pH, thereby inhibiting the occurrence of HER and promoting the production of multicarbon products⁶⁶. The low-coordinated copper on the rough surface may also have a positive effect on the catalytic activity⁶⁷⁻⁶⁸. It has been found that the oxidation-reaction cycles can efficiently roughen the Cu surface and be a robust method to prepare oxide-derived Cu catalysts for highly efficient CO₂RR⁶⁹⁻⁷¹.

Another promising pathway is to modulate the catalyst local microenvironment through surface interactions with molecular additives. As discussed in section 1.3.2, an important role of OH⁻ over Cu surface is to tune the surface Bader charge and stabilize CO₂RR intermediates, which opens the door to other molecular adsorbates potentially playing similar roles, perhaps more effectively. For instance, coupling pyridinium-derived dimers to a Cu surface in GDE greatly boosts ethylene selectivity in neutral media⁷². A different approach is to use molecular modification to change the interfacial microenvironment at the metal surface. This idea is inspired by the specific selectivity of enzymes in bacteria, which exhibit ultra-high selectivity toward specific products during CO₂RR.⁷³ Along these lines, it has been found that by tuning the ordering/disordering of the ligands shell, the catalytic performance on Cu can also be rationally tuned⁷⁴.

All the above CO₂RR catalytic strategies discussion are solely based on Cu. However, although Cu can effectively catalyze the C-C coupling process, it is not an optimum catalyst for CO production, which is widely regarded as the most important intermediate in multicarbons generation. Therefore, adding a second component that is efficient for CO generation to further tune the complex carbon dioxide process without changing the Cu surface features is also a very promising design principle for catalytic systems. Theoretically, this tandem strategy is on another dimension of system optimization and therefore is compatible with all the previously discussed Cu catalyst development

strategies. Various systems, such as Cu-Au⁷⁵⁻⁷⁶, Cu-Ag⁷⁷⁻⁷⁹, Cu-Pd⁸⁰, and Cu-Ni single atom catalysts⁸¹ have been developed targeting a better multicarbon production rate and selectivity. Since Au and Cu are relatively easy to form alloys during electrolysis, Cu and Ag are the most welcomed combinations due to the high CO selectivity on Ag-based catalysts.

In subsequent chapters of this dissertation, the main focus is put on the development of the tandem strategy and the catalyst structural evolution and molecule transformation mechanisms in tandem systems.

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Chapter 2 Cu-Ag Tandem Catalysts for High-Rate CO₂ Electrolysis towards Multicarbon

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2.1 Introduction

CO₂ electrolysis is a promising technique for CO₂ recycling and utilization¹⁻², offering carbon-neutral chemical feedstocks³ for downstream applications. Electrochemical CO₂RR towards single carbon products has achieved enormous progress⁴, especially for carbon monoxide⁵⁻⁹. However, in the periodic table, copper (Cu) is the only metal that can efficiently catalyze CO₂ to multicarbon products (C₂H₄, C₂H₅OH, CH₃COOH, n-C₃H₇OH, etc.), which was firstly reported by Hori and co-workers¹⁰. Since multicarbon products are higher-value and energy concentrated^{1,3}, widespread attention is paid to the unique catalytic property of the Cu surface. Both theoretical¹¹ and experimental¹² works demonstrate that sluggish C-C coupling kinetics over a pure Cu surface impedes industrial level production of multicarbon products. Thus, various multicomponent catalyst design principles have been utilized to improve the catalytic performance of Cu-containing catalysts, such as alloy formation¹³⁻¹⁵, surface doping¹⁶⁻¹⁷, ligand modification¹⁸⁻²⁰, and interface engineering²¹⁻²⁴.

One attractive multicomponent strategy is to break down the multiple reaction steps of CO₂-to-C₂₊ to have optimized components perform each step. In recent years, this “tandem catalysis” strategy has been successfully demonstrated in thermal heterogeneous catalysis²⁵⁻²⁷. Since it has been widely accepted that *CO (* denotes surface adsorbed species) and CO related intermediates are critical for CO₂RR towards multicarbons^{4, 28-29}, the tandem strategy is also suitable for CO₂ electrolysis. Due to excellent CO formation ability over Ag and Au, Cu-based bimetallic tandem platforms have been invoked for CO₂RR³⁰⁻³⁴. However, the practicality of such a strategy at high production rates (*i.e.* > 200 mA/cm²) is still in question, due to CO₂ mass transport limitations in previous works. The gas diffusion electrode (GDE) can eliminate sluggish feed gas transportation kinetics by constructing an efficient three phase interface³⁵⁻³⁶. Nevertheless, the micro-environment around the catalyst may be considerably different during high-rate electrolysis compared with aqueous conditions³⁷. Thus, to establish decoupled electrocatalytic CO₂-to-C₂₊ paradigms in high-rate electrochemical environments, the efficacy of a tandem platform should be evaluated in a gas diffusion electrode flow cell.

Here, in order to evaluate whether a tandem strategy can be utilized in high-rate CO₂ reduction, we designed a model two-component catalytic architecture in alkaline

electrolyte with commercial Cu and Ag powder (Figure 2.1a). Ag is selected for its high activity for CO formation during CO₂RR³⁸ and its thermodynamically immiscible nature with Cu at room temperature, thereby deconvolving enhancement due to bulk elemental alloying³⁹. Although 1M KOH electrolyte is ultimately unsustainable for long term practical electrolysis due to electrolyte instability from reaction with CO₂, it is useful as a model environment to evaluate catalytic concepts at the early stage³⁷. Compared against Cu alone, a significant enhancement of the partial current towards C₂₊ products (C₂H₄, C₂H₅OH, CH₃COOH) is observed over the tandem catalyst during CO₂ electrolysis, with a concurrent selectivity shift towards oxygenates over C₂H₄. Both post-electrolysis characterization and electrochemical CORR results confirm that the active sites over Ag and Cu surfaces work independently during CO₂RR, supporting the importance of a CO-rich local environment generated by the Ag component for enhancing C-C coupling on the Cu component in accordance with the tandem strategy. Furthermore, the normalized intrinsic activity towards C₂₊ products indicates that the Ag-generated microenvironment in tandem CO₂RR is superior to both pure CO₂ and CO atmosphere for Cu-catalyzed multicarbon production. This phenomenon suggests the existence of mechanisms for CO₂ reduction enhancement specifically stemming from tandem strategies and their resulting chemical microenvironments.

2.2 Experimental method

Materials: Commercial Cu powder (40-60 nm particle size (SAXS)), commercial Ag powder (<100 nm particle size), deuterium oxide (D₂O, 99.9 atom % D), dimethyl sulfoxide (DMSO, ACS reagent, ≥99.9%) and Nafion 117 ionomer solution (~5% in water and alcohol mixture) was purchased from Sigma-Aldrich. KOH pellets (>85%) were purchased from Fisher Chemicals. Anion exchange membrane (Fumasep FAA-3-PK-130) and Sigracet carbon papers were ordered from Fuel Cell Store. Ag/AgCl (3M KCl) reference electrodes were purchased from CH Instrument. Platinum gauze (99.9% metal basis) was purchased from Alfa Aesar. Carbon dioxide (CO₂, 4.5LS), carbon monoxide (4.0 research) and Argon gas were purchased from Praxair. Deionized water (DI water with 18.2 MΩ·cm, <5 ppb TOC) was obtained from a Millipore water system.

Electrode preparations: The following procedures describe the fabrication of a Cu₅₀₀Ag₁₀₀₀ catalyst, with other catalysts produced in a similar fashion and adjusting for mass. 12 mg commercial Cu or Ag nano-powder was firstly mixed with 4 ml ethanol, 40 µl Nafion ionomer solution and then sonicated for 1h in the water bath to produce a uniform ink. Cu and Ag inks were mixed together with 1:2 volume ratio and then spray-cast on carbon paper with a spray gun (SPEEDAIRE, Mod. 48PX90). After that, the fabricated electrode was stored in a vacuum desiccator overnight to remove residual ethanol. Cu₅₀₀Ag₁₀₀₀ represents a Cu-Ag tandem catalyst with 500 µg/cm² Cu and 1000 µg/cm² Ag theoretically. The weight difference of carbon paper before and after spraying was measured by an analytical balance to confirm the loading amount.

Characterization: The image of Cu and Ag powder morphology was collected by transmission electron microscopy (Tecnai G2 T20 S-TWIN) under 200 kV. Scanning Electron Microscopy (Ultra 55-FESEM) is operated at 5 keV with a 5 mm working

distance to characterize the fabricated electrode morphology and elemental distribution before and after electrolysis. XRD (Bruker D8) patterns were collected using a Cu target. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha) measurement was conducted using an Al K α source. For all post-electrolysis samples, electrodes were taken after CO₂ electrolysis at 200 mA/cm² constant current density for 30 min, then rinsed with deionized water and isopropanol repeatedly in order to remove as much electrolyte residue as possible and dried in a vacuum desiccator before measurement.

Electrochemical experiments and product quantification: All CO₂ and CO involved electrolysis was conducted in a gas diffusion flow cell. Before electrolysis, the electrolyte was firstly bubbled with argon for at least 30 min to remove dissolved oxygen. In this work, 1 M KOH was used as the electrolyte. The gas flow rate during electrolysis was controlled by a mass flow controller at 25 sccm while the electrolyte flow rates in cathode and anode channels were managed by two low-flow chemical metering pumps at 5 ml/min. The flow-out electrolyte would be directly collected for product analysis or transferred to a waste bottle instead of feeding back to the cell in order to eliminate pH drop induced by the neutralization reaction between KOH and CO₂. During all electrolysis, the cathode and anode were separated by a Fumasep anion exchange membrane. Ag/AgCl (3M KCl) was used as the reference electrode. Considering batch-to-batch difference and harsh working conditions (high current and high pH), the Ag/AgCl reference electrode was frequently calibrated and replaced if needed.

During chronopotentiometry (CP), both gas and liquid products were collected and analyzed. Sampling was conducted at least 300 s after the electrolysis began in order to let the system reach a steady state. No automatic iR correction was applied during CP experiments. After product collection, the cathodic potential and resistance between the working electrode and reference electrode were precisely measured by a subsequent current interrupt (CI) experiment. The back-calculated potentials were based on equation 2.1:

$$E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + iR + E_{\text{Ag/AgCl vs RHE}} \quad (2.1)$$

The RHE potential is calculated using a pH value of 14. After electrolysis, gas products, including CO, CH₄, C₂H₄ and H₂ were detected and quantified using gas chromatography (Agilent 7890B GC system). Three GC columns (1.5 ft HayeSep Q, 6 ft HayeSep Q and 6 ft Molsieve 5A) are used to separate different gases. CO and CO₂ were additionally transformed into CH₄ with a methanizer. H₂ was detected by TCD (Ar flow) while other gases were detected by FID. Liquid products were analyzed by ¹H nuclear magnetic resonance (Bruker AV600 with a 5 mm Z-gradient triple resonance ¹H/BB Prodigy cryo-probe) with water suppression by excitation sculpting. DMSO was used as an internal standard for quantitative NMR. Through the calibration curve, the concentration of the products can be determined (unit: mM for liquid products and ppm for gas products). The partial current density of the products can be calculated with the equations 2.2 and 2.3

$$j_{\text{gas product}} = c_{\text{gas product}} \times 10^{-5} \times e^{-} \text{ transfer number} \times F \times v_{\text{gas}} / (V_m \times S) \quad (2.2)$$

$$j_{\text{liquid product}} = c_{\text{liquid product}} \times e^- \text{ transfer number} \times F \times v_{\text{electrolyte}} / S \quad (2.3)$$

where:

j : partial current density (mA/cm²)

c : concentration of the product in gas phase (ppm) or electrolyte (M)

F : Faraday constant (96485 C/mol)

v : flow rate (mL/s)

V_m : molar volume at room temperature and pressure (293 K, 1 atm)

S : electrode geometric area (cm²)

Subsequently, faraday efficiency (FE) can be obtained with:

$$FE = j_{\text{product}} / j_{\text{total}} \times 100\% \quad (2.4)$$

Specifically, in this work, enhancement factor (EF) at specific potentials was defined as:

$$EF = j_{\text{product on tandem catalyst}} / j_{\text{product on single Cu catalyst}} \quad (2.5)$$

And normalized intrinsic activity towards multicarbons was calculated with the equation 2.6:

$$\text{normalized intrinsic activity} = j_{\text{product}} / (F \times e^- \text{ transfer number} \times d_{\text{Cu}}) \quad (2.6)$$

where:

d_{Cu} : Cu loading density (mg/cm²)

2.3 Structural characterization of Cu-Ag tandem electrode

A Cu-Ag tandem architecture catalyst was prepared by physical mixture of Cu and Ag nano powders on carbon paper support and utilized in gas diffusion flow cells (Figure 2.2) for high current CO₂ electrolysis. The morphology of commercial Cu and Ag powders is revealed with TEM (Figure 2.3), showing that the crystalline feature size of both Cu and Ag is tens of nanometers, but heavily agglomerated with no distinct morphology. The electrode fabricated with these metal powders was named as Cu_xAg_y, representing a Cu-Ag tandem catalyst with $x \mu\text{g}/\text{cm}^2$ Cu and $y \mu\text{g}/\text{cm}^2$ Ag respectively (see experimental procedures). Then, these electrodes were imaged under SEM. The thickness of the catalyst layer in the as-prepared Cu₅₀₀Ag₁₀₀₀ catalyst on carbon paper is several microns (Figure 2.1b, c). SEM after electrolysis shows no significant structural change on the micron scale from the initial structure (Figure 2.4).

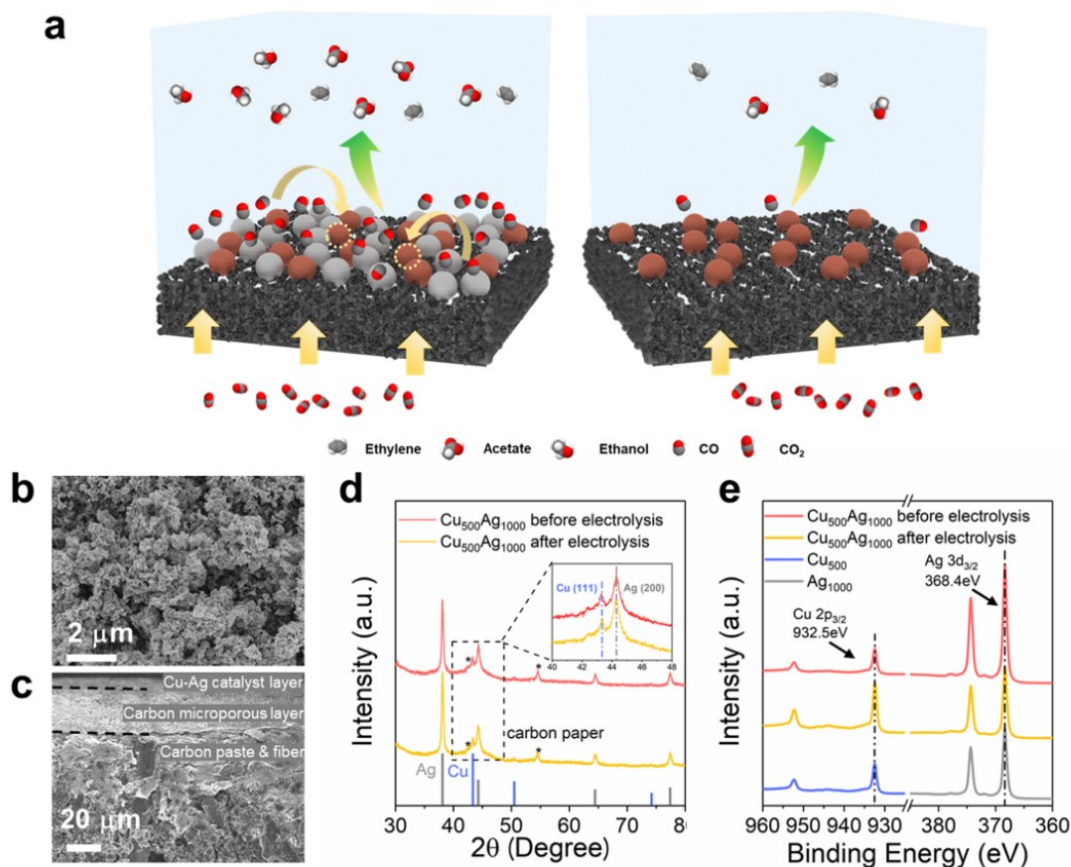


Figure 2.1. Cu-Ag tandem architecture design and characterizations. (a) Scheme of the Cu-Ag tandem platform for high rate CO₂ electrolysis and C₂⁺ products formation. (b) Top view SEM image of Cu₅₀₀Ag₁₀₀₀ catalyst over carbon paper before electrolysis. (c) Cross-section SEM image of Cu₅₀₀Ag₁₀₀₀ catalyst over carbon paper before electrolysis. (d) XRD patterns of Cu₅₀₀Ag₁₀₀₀ catalyst over carbon paper before and after electrolysis. Inset: Cu(111) and Ag(200) range enlarged. Standard PDF index of Cu (ICDD PDF# 99-0034) and Ag (ICDD PDF# 99-0094) are plotted for comparison. (e) XPS spectrum of Cu₅₀₀Ag₁₀₀₀ catalyst over carbon paper before and after electrolysis, with Cu₅₀₀ and Ag₁₀₀₀ for comparison. Post-electrolysis samples were prepared after conducting CO₂RR at 200 mA/cm² constant cathodic current density for 30 min.

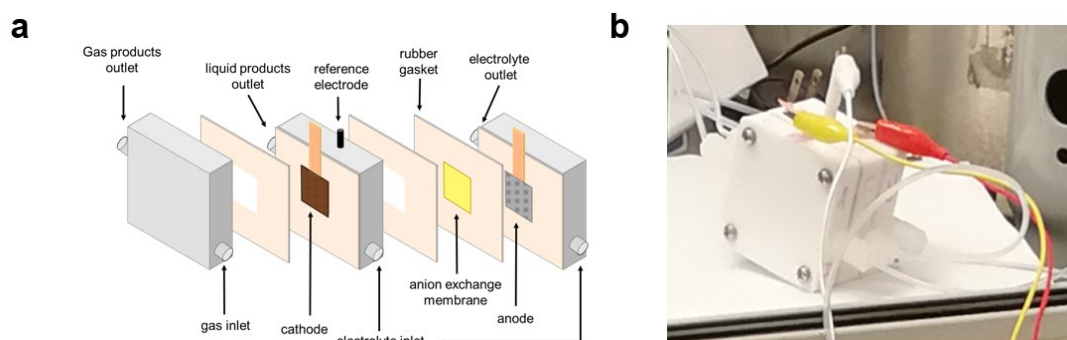


Figure 2.2. Gas diffusion cell configuration used in this work. (a) schematic illustration and (b) photograph.

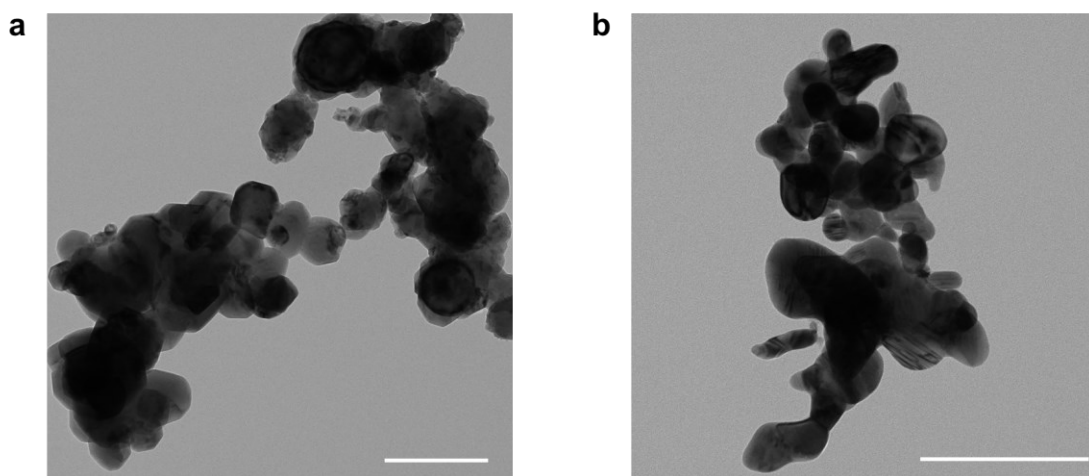


Figure 2.3. Additional morphology characterization of commercial Cu and Ag powders. (a) TEM image of commercial Cu (b) TEM image of commercial Ag. Scale bar: 200 nm.

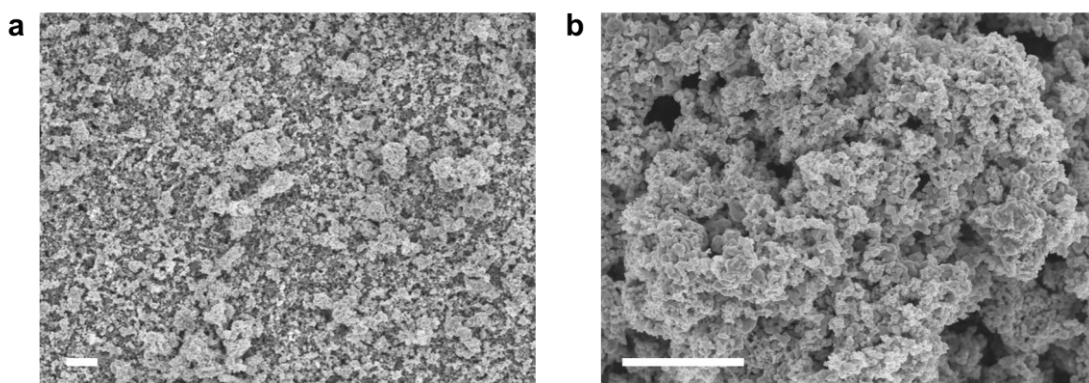


Figure 2.4. SEM image of tandem Cu₅₀₀Ag₁₀₀₀/carbon paper after electrolysis. (a) low magnification and (b) high magnification SEM image of tandem Cu₅₀₀Ag₁₀₀₀ catalyst after CO₂ electrolysis (30 min, 200 mA/cm², 1M KOH electrolyte). Scale bar: 2 μm.

Elemental characterization through XRD, XPS and EDS mapping (Figure. 2.1d and e, Figure 2.5) provides further insight into the nature of the tandem catalyst. Both XRD patterns and XPS spectra of the as-prepared tandem $\text{Cu}_{500}\text{Ag}_{1000}$ catalyst show characteristic Cu and Ag related peaks without any observable peak shifting. Although the Cu LMM Auger peak indicates that the surface of nano powder has been oxidized, numerous studies⁴⁰⁻⁴⁴ indicate that such a naturally formed oxide shell can be quickly reduced under working conditions. Despite the ongoing debate in the community towards the existence and function of oxygen residue during CO_2RR ⁴⁵⁻⁴⁷, we note that such a phenomenon will not influence the conclusions related to tandem interactions between Ag and Cu in the later discussion in this work. Meanwhile, it is widely reported that Cu can undergo surface reconstruction and structural evolution during CO_2 electrolysis,⁴⁸⁻⁵¹ and previous reports have also invoked Cu-Ag alloy¹³⁻¹⁵ or surface alloy¹⁶ strategies to improve CO_2RR catalytic performance. Thus, we conducted post-electrolysis characterization of the tandem $\text{Cu}_{500}\text{Ag}_{1000}$ catalyst to determine whether the structure is maintained. Previous works have shown structural and electronic differences owing to strong Ag interactions with Cu: for example, up to 0.8° Cu(111) peak shift in XRD could be found for a Cu-Ag alloy system¹⁴ whereas up to 0.3 eV Cu 2p_{3/2} peak shift in XPS was reported for a Cu-Ag dimer.²³ In contrast, no peak shift of Cu or Ag could be observed for the tandem $\text{Cu}_{500}\text{Ag}_{1000}$ catalyst in either XRD, XPS or Cu LMM Auger peak after electrolysis, indicating the structural maintenance of this tandem catalyst and the absence of electronic interactions between Ag and Cu throughout electrolysis. This absence is likely due to the bulk-like nature of Ag and Cu used, in addition to the mild conditions in which the electrode is fabricated, resulting in thermodynamically favored separation⁵². Importantly, this does not preclude the Ag-Cu surface and interfacial alloying observed in other reports which use more energetic fabrication conditions.

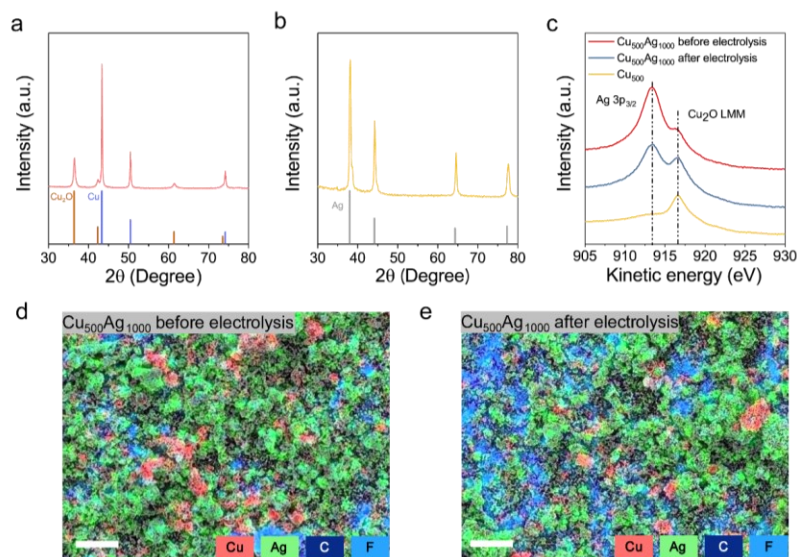


Figure 2.5. Supplementary elemental characterization data. (a) commercial Cu and (b) commercial Ag. Standard PDF index of Cu (ICDD PDF# 99-0034), Cu_2O (ICDD PDF#

99-0041), Ag (ICDD PDF# 99-0094) were also plotted for comparison. (c) LMM auger spectrum of tandem catalyst before and after electrolysis. Pure Cu catalyst was also characterized for reference. The auger peak of Cu₂O is partially overlapped with Ag 3p_{3/2}. Both XRD and XPS data confirm the existence of Cu₂O at the particle surface, likely due to surface oxidation. Elemental mapping of tandem Cu₅₀₀Ag₁₀₀₀ catalyst (c) before and (d) after CO₂ electrolysis. Scale bar: 5 μm. Based on EDS elemental mapping, Cu and Ag powder was mixed at the micron level, which is consistent with the TEM image in Fig S2. For Cu₅₀₀Ag₁₀₀₀ catalyst, it can be observed that Cu and Ag are segregated both before and after CO₂ electrolysis. This offers additional supporting evidence for confirming the lack of bulky alloy formation.

2.4 Enhanced CO₂RR catalytic performances toward multicarbon products over tandem Cu-Ag catalysts

The polarization response curve of Cu₅₀₀Ag₁₀₀₀ in Figure 2.6a shows a higher geometric current density than Cu₅₀₀ or Ag₁₀₀₀ alone under the same potentials. Interestingly, partial current densities toward C₂₊ products over different catalysts are also observed to be substantially higher for Cu₅₀₀Ag₁₀₀₀, which cannot be explained simply through the individual contributions of Cu₅₀₀ and Ag₁₀₀₀ (Figure 2.6b). Explicitly, Ag₁₀₀₀ does not contribute to C-C coupling reactions in the potential range from -0.5 V to -0.8 V vs RHE. Thus, all partial current toward C₂₊ products should come from the Cu surface. Based on linear interpolation, the partial current toward C₂₊ products over Cu₅₀₀ surface is only about 37 mA/cm² at -0.70V, while the corresponding C₂₊ partial current density over Cu₅₀₀Ag₁₀₀₀ is 160 mA/cm². As the theoretical Cu loading density is constant between Cu₅₀₀ and Cu₅₀₀Ag₁₀₀₀, the significant enhancement of the C₂₊ partial current density over the tandem catalyst beginning at around -0.55 V vs RHE should be attributed to the additionally loaded Ag. The enhancement of C₂₊ products is shown to be dependent on the extent of Ag loading (Figure 2.7), further reinforcing that Ag is responsible for the increase in C₂₊ production.

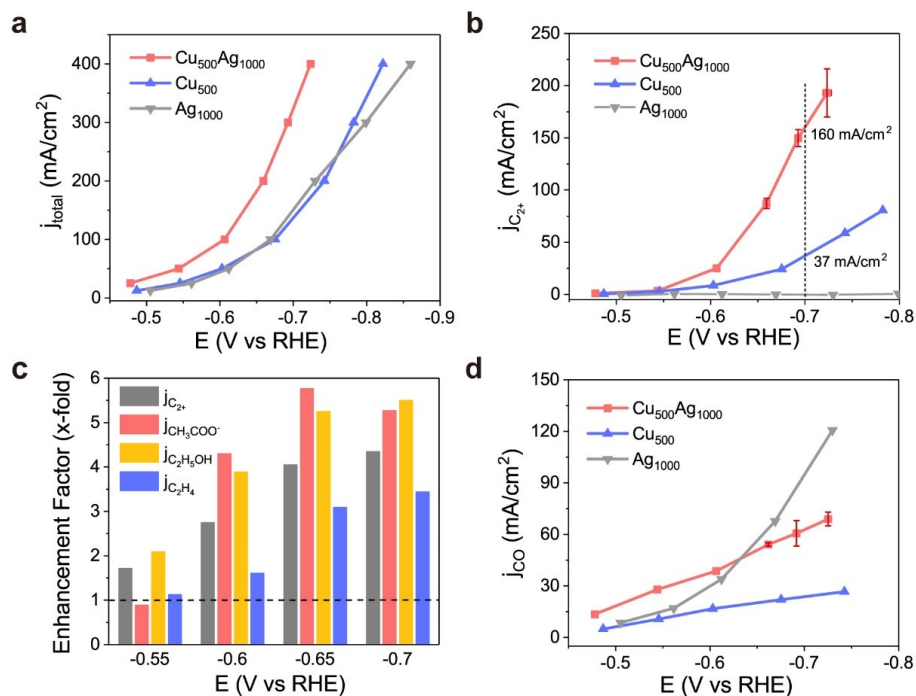


Figure 2.6. CO₂RR performance of tandem catalysts comparing with pure metal catalysts. (a) Total geometric current density curve of Cu₅₀₀Ag₁₀₀₀, Cu₅₀₀ and Ag₁₀₀₀ catalysts. (b) Partial current density towards C₂⁺ products over Cu₅₀₀Ag₁₀₀₀, Cu₅₀₀ and Ag₁₀₀₀ catalysts. (c) Enhancement factors (EF) for total C₂⁺ and individual products over four different potentials (-0.55V, -0.60V, -0.65V and -0.70V vs RHE) in CO₂RR, which is defined as the tandem Cu₅₀₀Ag₁₀₀₀ partial current divided by that of Cu₅₀₀ catalyst alone. Linear interpolation was used to obtain the estimated current values at these potentials. (d) CO production partial current density over Cu₅₀₀Ag₁₀₀₀, Cu₅₀₀ and Ag₁₀₀₀ catalysts. Data points with error bars (1 SD) in all figures are based on the average value of three separate experiments results.

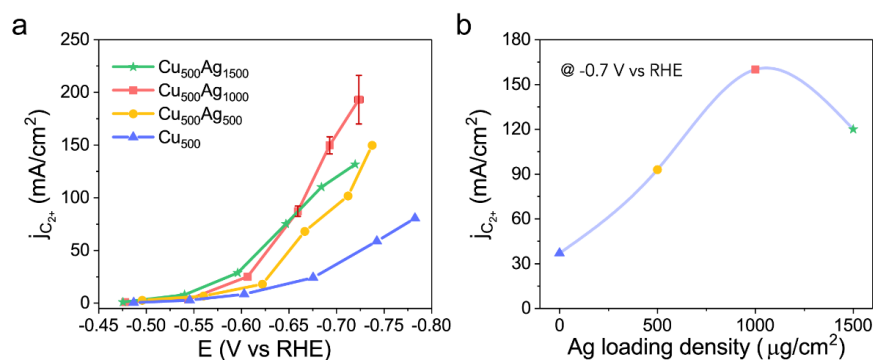


Figure 2.7. Ag-loading dependent catalytic performance towards multicarbons over tandem catalysts. (a) Partial current density towards C₂⁺ products over tandem

Cu₅₀₀Ag₁₅₀₀, Cu₅₀₀Ag₁₀₀₀, Cu₅₀₀Ag₅₀₀ and Cu₅₀₀ catalysts in CO₂RR. Data points with error bars (1 SD) based on the average value of three separate experiments results. (b) The relationship between Ag loading density in tandem catalyst and partial current density towards C₂₊ products at -0.70 V vs RHE. Partial current density values at -0.70 V vs RHE were obtained by linear interpolation. While Ag loading density is below 1000 µg/cm², higher loading will result in a larger C₂₊ partial current. But when Ag loading density exceeds 1000 µg/cm², no further promotion could be observed, which may due to blockage of available Cu sites due to overcrowding of Ag.

C₂₊ partial currents are further broken down to their main constituents to analyze how the tandem strategy influences product distribution (Figure 2.6c). Here we define the enhancement factor (EF) as the tandem Cu₅₀₀Ag₁₀₀₀ partial current divided by that of the Cu₅₀₀ catalyst alone. Beginning from -0.55 V vs RHE, the EFs of C₂H₄, C₂H₅OH and CH₃COO⁻ all increase significantly when the applied potential is more negative (Figure 2.6c). Thus, a relatively negative potential is essential to trigger the Ag-derived C₂₊ enhancement, achieving up to 6.43, 11.27, and 16.22 µg/h·cm²_{geom} production rates toward C₂H₄, C₂H₅OH and CH₃COO⁻ respectively over the Cu surface. Furthermore, oxygenate products are favored over C₂H₄ on the tandem catalyst, consistent with previous reports that invoke enhancement by local CO concentration^{31, 51}. At -0.70 V vs RHE, the EFs are mostly at the same range as -0.65 V vs RHE, indicating that the tandem strategy induced enhancement is limited by factors beyond potential, such as the concentration of CO local to the catalyst. Similar trends can also be observed from tandem catalysts with other Cu-Ag ratios (Figure 2.8).

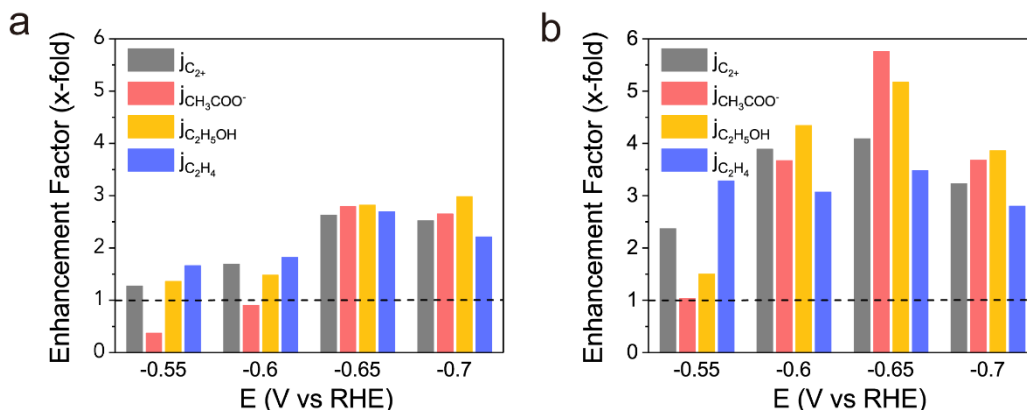


Figure 2.8. Enhancement factors (EF) between (a) Cu₅₀₀Ag₅₀₀ and Cu₅₀₀ (b) Cu₅₀₀Ag₁₅₀₀ and Cu₅₀₀ during CO₂RR, which is defined as the quotient of the partial currents between two catalysts. Both total and specific C₂₊ products (C₂H₄, C₂H₅OH, CH₃COO⁻) EFs were calculated over four different potentials (-0.55V, -0.60V, -0.65V and -0.70V vs RHE). Linear interpolation was used to obtain the estimated current values at these potentials.

To further probe the role of local CO towards the C_{2+} enhancement, the net CO producing abilities of these catalysts are also compared (Figure 2.6d). At potentials negative of -0.5 V vs. RHE, the C-C coupling reaction dominates such that net CO production rate over Cu_{500} remains at a relatively low level within the potential range. Meanwhile, Ag exhibits an exponential increase in CO production with respect to overpotential. Notably, the onset potential for C_{2+} enhancement is around -0.55 V vs RHE, where CO partial current on the pure Ag_{1000} catalyst is observed to take off. This indicates a direct correlation between C_{2+} enhancement on the $Cu_{500}Ag_{1000}$ catalyst and net CO production rate. Hence, the partial C_{2+} current enhancement is attributed to the high local CO created on the Ag surface within the tandem catalyst layer. Interestingly, Clark et al. invoked that the enhanced oxygenates selectivity is not attributed to localized CO produced by Ag, but by strain effects induced by surface Ag doping which modulates C-C coupling activity and suppresses HER.¹⁶ Similarly, such HER suppression and oxygenates favoring phenomenon were also observed in other Cu-Ag alloy catalysts¹⁴⁻¹⁵. The differing contributions of tandem effects on catalysis (*i.e.* whether localized CO may influence further C_{2+} activity) between this work and previous works mentioned above may be due to the difference in the electrolyte. It has been reported that high pH electrolyte can significantly accelerate C-C coupling reaction over Cu surface³⁶, which would correspond to the more efficient utilization of CO in our system. Notably, the correlated suppression of HER typically observed from Ag-alloying or doping is not found in our system (Figure 2.9), suggesting that the Ag doping effect is mostly negligible here and that the intrinsic catalytic activity of Cu is not influenced by Ag atomic interactions. More contextualization and comparison of relevant works can be found in Figure. 2.10 and Table 2.1.

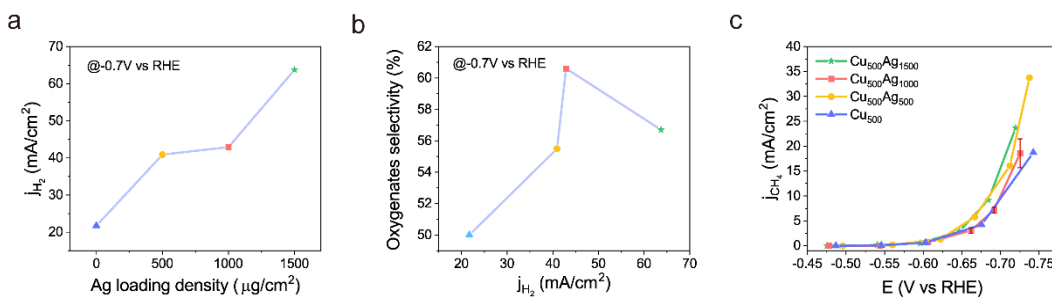


Figure 2.9. Ag-loading dependent catalytic performance towards minor products over tandem catalysts. (a) Partial current density towards H_2 over tandem $Cu_{500}Ag_{1500}$, $Cu_{500}Ag_{1000}$, $Cu_{500}Ag_{500}$ and Cu_{500} catalysts at -0.70 V vs RHE in CO_2RR . (b) The relationship between HER partial current density in tandem catalyst and oxygenates selectivity in multicarbon products at -0.70 V vs RHE. Partial current density values at -0.70 V vs RHE were obtained by linear interpolation. Generally, these results do not support a negative correlation between oxygenates selectivity and HER partial current density, which has been previously observed in Ag doped Cu catalyst¹⁶. Instead, a positive correlation can be found between Ag loading density and HER partial current density, suggesting a different mechanism for C_{2+} enhancement in this work relative to

Ag-doped Cu works. (c) Partial current density towards CH₄ over tandem Cu₅₀₀Ag₁₅₀₀, Cu₅₀₀Ag₁₀₀₀, Cu₅₀₀Ag₅₀₀ and Cu₅₀₀ catalysts in CO₂RR. Data points with error bars (1 SD) based on the average value of three separate experiments results. The methane production rate seems to be independent with Ag loading density, which may suggest that methane production is not CO-limited.

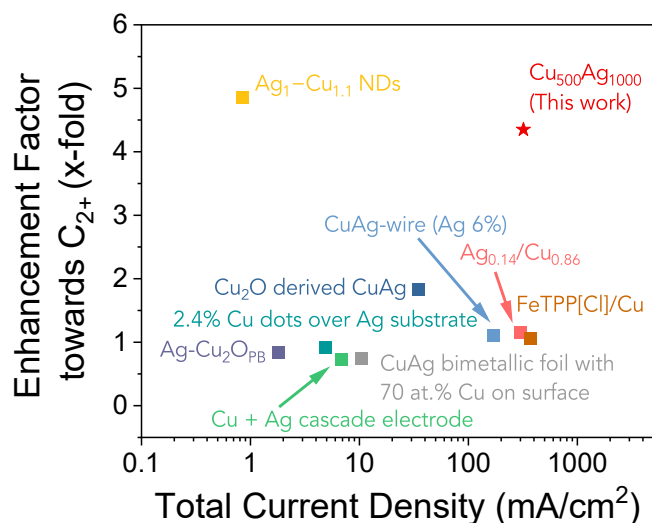


Figure 2.10. Contextualization and comparison with relevant literature. Total current density under most representative potential and the enhancement factors towards multicarbons are used as two indicators for comparison. More detailed information, including electrolyte, potential, total current density value and enhancement factors towards specific multicarbon products, can be found in table 2.1.

Although the alloying strategy (CuAg bimetallic foil; Ag_{0.14}/Cu_{0.86}; Ag-Cu₂OPB) is a promising technique for tuning the selectivity of multicarbons, due to blockage of the surface, the value of EF towards total multicarbons are all around 1. Instead, tandem catalysts have a better potential to further improve EF (e.g. Cu₂O derived CuAg). We attribute a higher EF in our work to the efficient CO-generating component in the catalyst (as compared with FeTPP[Cl] as an example) and high surface pH derived from electrolyte species and high electrolysis rate.

Note: (1) Enhancement factor (EF) here is defined as the quotient of partial current density between composed catalyst with reference pure Cu catalyst in literature. Due to the varied morphology, ECSA and loading density of the reference catalyst compared with the composed catalyst in some literature, we remind readers of the potential imprecision contained in the calculated EF. (2) For the catalyst of Ag_{0.14}/Cu_{0.86}, offered comparison data are based on the same current density instead of the same potential. (3) Due to the lack of the same potential data, the product distribution under -0.84 V instead of -0.82 V vs RHE is used for the reference catalyst of FeTPP[Cl]/Cu.

Table 2.1. Catalytic performance and enhancement factor comparison of relevant literature. The values of current densities were either offered in literature or extracted from the corresponding figures. The bottom half of the table represents GDE works whereas the top half represents H-cell.

Catalyst	Electrolyte	Potential (V vs RHE)	Total current density (mA/cm ²)	Enhancement factor			
				C ₂ H ₄	C ₂ H ₅ OH	CH ₃ COOH & CH ₃ CHO	Total C ₂ +
CuAg bimetallic foil with 70 at.% Cu on surface ¹⁶	0.1 M CsHCO ₃	-1.05	10.1	0.6	1.2	4.5	0.8
Cu + Ag cascade electrode ³²	0.1 M CsHCO ₃	-1.0	6.9	0.4	1.4	1.2	0.7
Ag-Cu ₂ O _{PB} ¹⁵	0.2 M KCl	-1.2	1.8	0.3	1.9	0.9	0.9
2.4% Cu dots on Ag substrate ³¹	0.1 M KHCO ₃	-1.0	4.9	0.4	0.9	11.5	0.9
Cu ₂ O derived CuAg ³⁴	0.1 M KHCO ₃	-1.05	35.1	2.1	1.3	1.5	1.8
Ag ₁ -Cu _{1.1} NDs ²³	0.1 M KHCO ₃	-1.1	0.85	4.9	N.A.	N.A.	4.9
Ag _{0.14} /Cu _{0.86} ¹⁴	1 M KOH	N.A.	300	0.7	1.4	3.7	1.2
CuAg-wire (Ag 6%) ¹³	1 M KOH	-0.6	170	1.3	0.9	0.8	1.1
FeTPP[Cl]/Cu ²⁹	1 M KHCO ₃	-0.82	375	0.8	1.4	1.0	1.1
Cu ₅₀₀ Ag ₁₀₀₀ (This work)	1 M KOH	-0.7	320	3.4	5.5	5.3	4.4

2.5 Active site analysis and performance comparison based on CORR

Considering the importance of localized CO produced by the Cu-Ag tandem platform toward high rate C₂⁺ chemicals production, we next investigated how such platforms

behave under CO reduction reaction (CORR) conditions. If the addition of Ag electronically influences Cu active sites, we expect that CO reduction activity should differ between Cu and Cu-Ag catalysts⁵³. However, in stark contrast to our previous observations in CO₂RR, the Cu₅₀₀Ag₁₀₀₀ catalyst exhibits neither an enhancement in the total current nor an enhancement in C₂₊ formation under CO-reducing conditions (Figure 2.11a and b, Figure 2.12). Thus, in both Cu₅₀₀Ag₁₀₀₀ and Cu₅₀₀ catalysts, only the Cu component conducts CORR. Meanwhile, no substantial enhancement is observed owing to the bimetallic platform in CORR across all multicarbon products, as shown explicitly in Figure 2.11c, suggesting that the Cu₅₀₀Ag₁₀₀₀ catalyst has no intrinsic enhancement in CO coupling compared with Cu₅₀₀ alone.

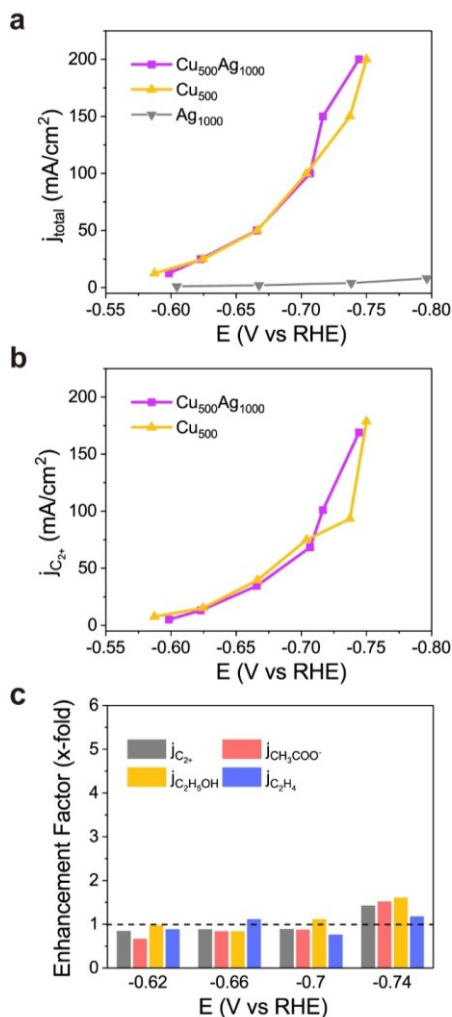


Figure 2.11. CORR performance of tandem catalysts comparing with pure metal catalysts. (a) Total currents of CO electroreduction reaction (CORR) over Cu₅₀₀Ag₁₀₀₀, Cu₅₀₀ and Ag₁₀₀₀ catalysts. (b) C₂₊ products partial currents of CORR over Cu₅₀₀Ag₁₀₀₀ and Cu₅₀₀ catalysts. (c) Enhancement factors (EF) for total C₂₊ and individual products

over four different potentials (-0.62V, -0.66V, -0.70V and -0.74V vs RHE) in CORR, calculated as described in Figure 2.6.

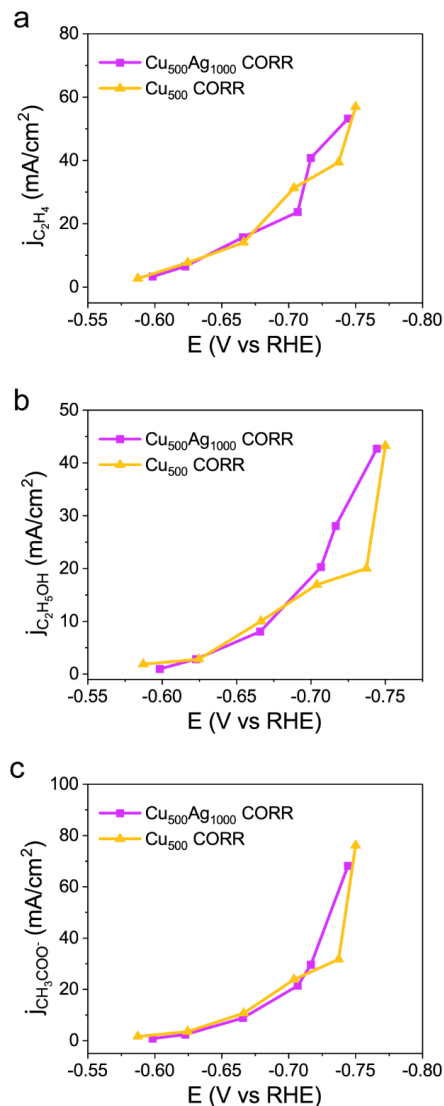


Figure 2.12. The partial current density of (a) C₂H₄, (b) C₂H₅OH and (c) CH₃COO⁻ over both tandem Cu₅₀₀Ag₁₀₀₀ and Cu₅₀₀ catalyst in CORR. No significant difference is observed.

In general, our CORR experiments strongly support the conclusion that Cu and Ag active sites operate independently. Ag produces CO from CO₂ and this generated CO in addition to the CO generated on Cu itself, is further utilized for multicarbon production over the Cu surface. In other words, we posit that in accordance with our structural

characterization, Ag does not modify the Cu surface during tandem CO₂RR. We note that although electrocatalytic activity changes over longer periods of electrolysis, this is due to commonly reported stability issues with flooding in carbon paper based gas diffusion electrodes^{36, 54-56}, rather than to structural changes of the catalyst (Figure. 2.13). Moreover, given the similar activity between Cu and Cu-Ag catalysts in CORR when catalyst preparation is simply normalized by Cu mass loading, we further hypothesize that intrinsic catalytic activity towards multicarbons can be internally compared using Cu mass normalization.

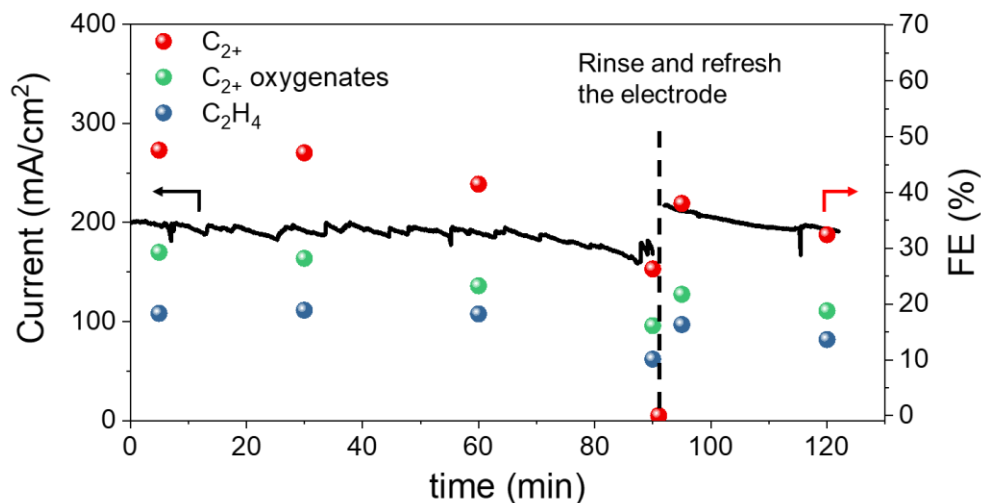


Figure 2.13. Stability test under constant applied potential with 200 mA/cm² as starting current density. The rapid catalytic deactivation happened after 1h electrolysis, which was mainly due to the severe flood in the gas diffusion layer. After the electrode was fully deactivated, it was rinsed with DI water to remove the electrolyte and precipitated out salts (*e.g.* K₂CO₃) thoroughly and then dried in the vacuum chamber. The recovered catalytic activity during resumed CO₂ electrolysis indicates the deactivation mostly due to the instability of the carbon paper and the accumulation of carbonate salts from KOH-CO₂ reactivity.

2.6 Intrinsic catalytic performances of Cu catalyst under different local environments

Considering the production rate normalized by the mass of Cu as a measure of intrinsic catalyst activity for internal comparison, we sought to determine how the local gas environments would influence the C₂₊ partial current over the Cu surface (Figure 2.14). Unsurprisingly, for CORR the activity towards all three main C₂₊ products over Cu₅₀₀ is larger than for CO₂RR. However, we also observed unexpectedly that the normalized C₂₊ partial current over tandem Cu₅₀₀Ag₁₀₀₀ during CO₂RR is beyond that of Cu₅₀₀ during

CORR. To exclude the influence of electron transfer differences in CO₂RR and CORR (e.g. for C₂H₄, 12e⁻ during CO₂RR, and 8e⁻ during CORR), we used the normalized intrinsic activity (in moles product per mass catalyst per time) to better represent the intrinsic performance over the Cu surface (Figure 2.15a-c). The normalized intrinsic activities of tandem Cu₅₀₀Ag₁₀₀₀ towards C₂H₄, C₂H₅OH, CH₃COO⁻ in CO₂RR are 3~6-fold larger than that of Cu₅₀₀ in CO₂RR at -0.7 V vs RHE. Moreover, the normalized intrinsic activities of tandem CO₂RR towards C₂H₄ and C₂H₅OH are still substantially larger than that of Cu₅₀₀ in CORR (Figure 2.15d), such that the local environment created by the tandem catalyst favors a greater overall formation for C₂₊ than CORR on Cu alone. Given that the role of Ag is to supply Cu with a CO-rich local environment, we considered how a similar amount of Cu in place of Ag would behave. The normalized catalytic activity over Cu₅₀₀Cu₁₀₀₀ is considerably lower than that of Cu₅₀₀Ag₁₀₀₀, likely due to the deficient CO₂-to-CO activity of a Cu surface per surface site. (Figure 2.16). Such results highlight the unexpected superiority of the tandem strategy for CO₂RR in a flow cell, which offers the opportunity to enhance the efficiency of C-C bonding on a Cu surface beyond conventional CORR during high-rate electrolysis.

The underlying mechanism accounting for this change in product distribution is also of interest. We find that the tandem-derived C₂₊ intrinsic activity enhancements over a Cu₅₀₀ surface can also be imitated with a blended gas of 2% CO and 98% CO₂ (Figure 2.17). Therefore, a mechanistic difference in mixed CO₂-CO atmosphere in the tandem catalyst layer may contribute to the enhancement of intrinsic activity towards a series of multicarbon products, similar to Strasser and co-workers' results in bicarbonate at lower electrolysis rates⁵⁷. Other factors in the double layer may also be involved. For example, a relatively low CO coverage over the Cu surface (2.5%~10% atm) can promote C₂H₄ formation rate during CORR⁵⁸ while *H coverage would influence C₂H₅OH formation during CO₂RR⁵⁹ by adsorbate-adsorbate interaction. Furthermore, the surface pH may also be an important influencing factor, due to subtle differences in the double layer given the presence of carbonate formation during CO₂RR³⁶. With many possible mechanisms for the enhancement observed under tandem Cu-Ag CO₂RR conditions, Cu catalysts with well-defined surfaces as well as advanced *in-situ* spectroscopy techniques for flow cells will be valuable future mechanistic tools.

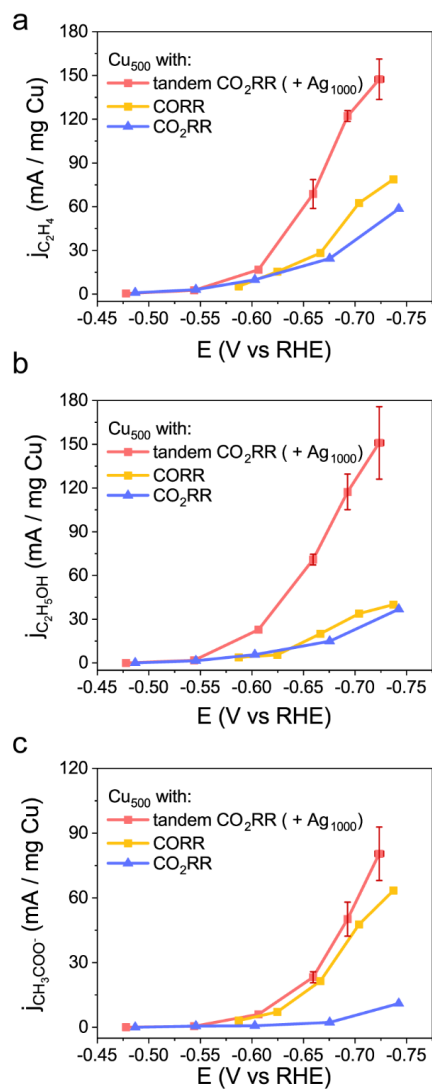


Figure 2.14. Normalized partial currents towards (a) C_2H_4 (b) C_2H_5OH (c) CH_3COO^- over Cu_{500} surface with different local environments. Data points with error bars (1 SD) in all figures are based on the average value of three separate experiments results.

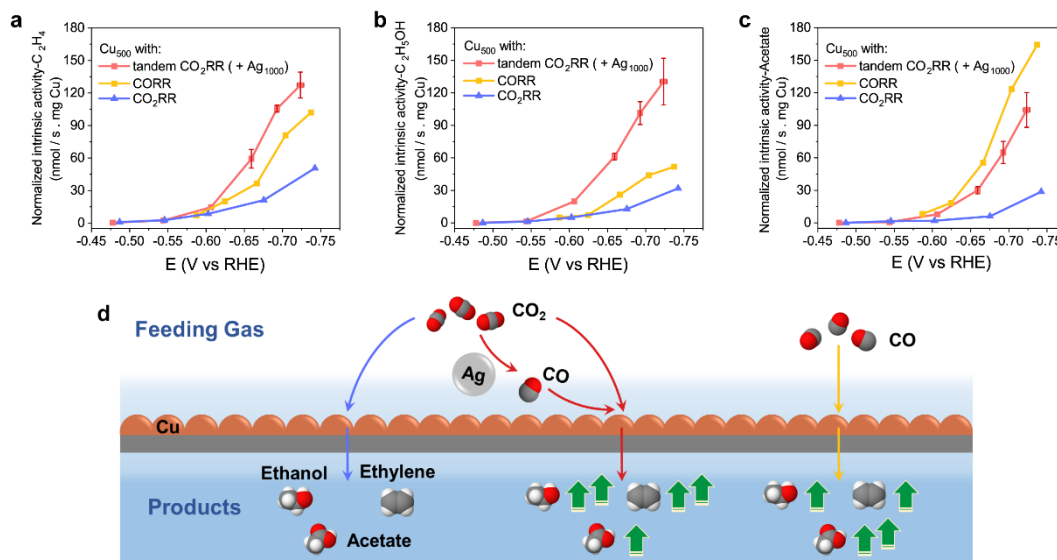


Figure 2.15. Normalized intrinsic activity analysis and corresponding schematic illustration. Normalized intrinsic activity towards (a) C_2H_4 (b) C_2H_5OH (c) CH_3COO^- over the Cu surface with different local environments (tandem CO₂ in red, fed CO in yellow, and fed CO₂ in blue). Data points with error bars (1 SD) in all figures are based on the average value of three separated experimental results. (d) Scheme representing the catalytic difference provided by the local environment produced by the tandem catalyst (red) vs. standard CORR (yellow) or CO₂RR (blue).

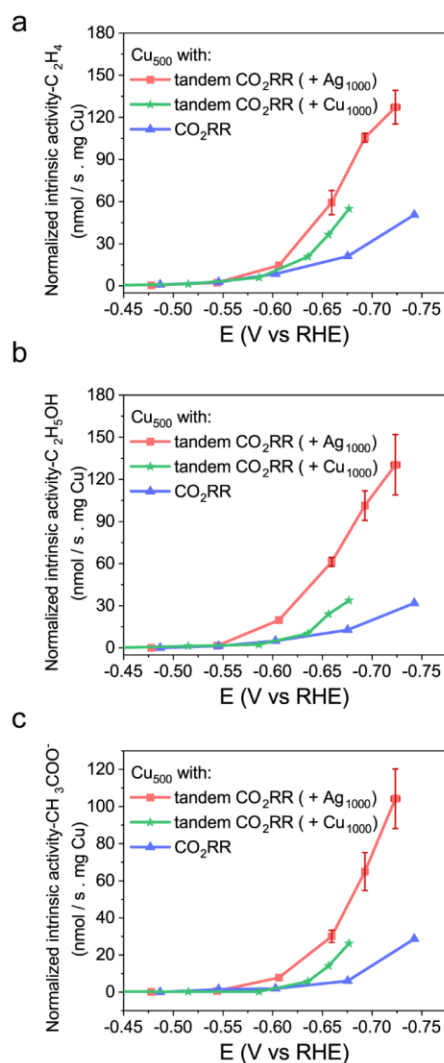


Figure 2.16. Normalized intrinsic activity towards (a) C_2H_4 (b) C_2H_5OH (c) CH_3COO^- over $Cu_{500}Cu_{1000}$ in CO_2RR . Cu_{500} and $Cu_{500}Ag_{1000}$ were also included for comparison. Data points with error bars (1 SD) in all figures are based on the average value of three separate experiments results.

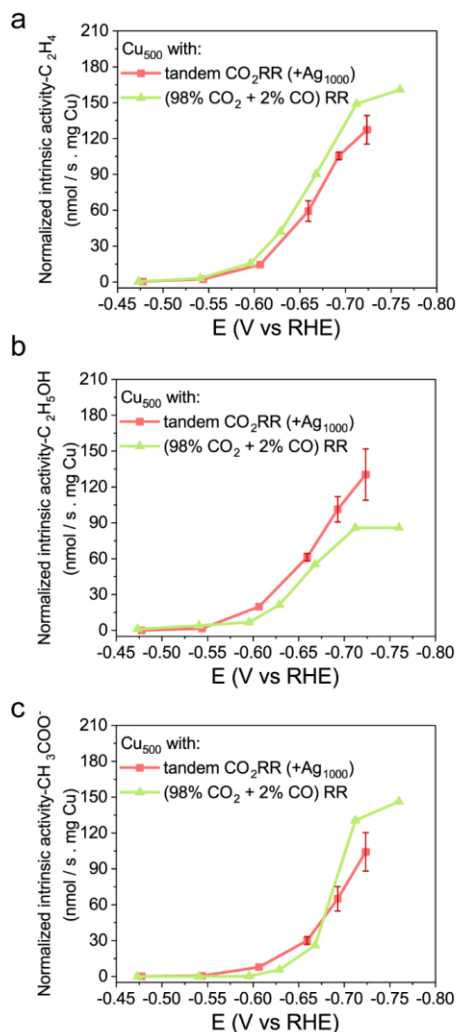


Figure 2.17. Imitating tandem catalytic performance with a mixed gas of 2% CO and 98% CO₂. Normalized intrinsic activity towards (a) C₂H₄ (b) C₂H₅OH (c) CH₃COO⁻ over Cu₅₀₀ in a mixed gas atmosphere with 98% CO₂ and 2% CO. Cu₅₀₀Ag₁₀₀₀ CO₂RR data were also included for comparison. Data points with error bars (1 SD) in all figures are based on the average value of three separate experiments results. Under comparable CO partial pressure, a similar intrinsic activity enhancement could also be observed on Cu₅₀₀, indicating the correlation between increased performance and the co-existence of CO and CO₂.

2.7 Conclusion

In this work, we established and evaluated a Cu-Ag tandem platform for achieving high current CO₂ electrolysis towards C₂⁺ products in a flow cell. In contrast with previous Cu-Ag works, Cu and Ag were confirmed to work independently in this system through post-electrolysis characterization and control experiments with CO reduction, such that the localized CO produced by Ag, with subsequent C-C bonding on Cu, is key towards

high rate C_{2+} production. Furthermore, we found over the same Cu surface, the turnover of C_2H_4 and C_2H_5OH in a tandem CO_2 -reducing platform is substantially higher than the activity for Cu in either pure CO_2 or pure CO-reducing conditions. Thus, we posit that the local environment created in high-rate tandem CO_2 electrolysis offers new opportunities for expanding the catalytic space of CO_2 electroreduction. Deep investigation of the local CO atmosphere *in situ* is required to further understand high-rate tandem CO_2 electrolysis.

Moreover, we emphasize that although a highly alkaline electrolyte is beneficial for new catalytic architecture exploration and demonstration, serious concerns remain regarding its sustainability and stability issues due to the reaction between KOH and CO_2 ³⁷. This may partially account for the lack of long-term stability observed in this work (Figure 2.13). Translating the catalytic concept demonstrated here to truly practical CO_2 electrolysis requires a systematic design that reduces CO_2 interaction with alkaline electrolytes while ideally still leveraging the catalytic benefits of local hydroxide. One avenue of interest may be to substitute bulk KOH electrolyte with local metal hydroxide at the cathode. Further exploration of catalyst design with cell engineering as a multi-scale strategy in sustainable electrolytes will undoubtedly be needed to enable practical tandem CO_2 electrolysis systems.

2.8 References

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Chapter 3 Structural Evolution of Cu-Ag Nanoalloys under Electrochemical CO₂RR

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3.1 Introduction

Carbon dioxide electrochemical reduction reaction (CO₂RR) draws broad attention due to its importance in the carbon neutrality effort. According to the anticipation of the International Energy Agency, 8% of the captured CO₂ by 2070 will be utilized for valuable chemical production.

As mentioned in Chapters 1 and 2, Cu is the only metal catalyst that can achieve efficient CO₂ to multicarbon transformation and therefore becomes an important catalytic system in electrochemical CO₂RR. However, the bare Cu system is not a satisfying metal catalyst for CO₂ to CO transformation and therefore influences the generation of multicarbon products¹. One promising strategy is to improve the catalytic activity and selectivity by constructing a hybrid system in which multi-component or multiple active sites co-exist².

Silver (Ag) is a promising secondary metal that is suitable to be added to the catalytic system due to its high efficiency to generate CO³ and also its thermodynamic immiscibility with Cu⁴. Therefore, great attention has been paid to the application of Cu-Ag bimetallic catalysts in CO₂RR. Based on different interactions between Cu and Ag, the Cu-Ag bimetallic catalysts can be roughly classified into three categories. Generally, without mutual interference, Ag can generate a CO concentrated local environment in electrochemical CO₂RR, which is then utilized by Cu catalyst and boost the multicarbon generation rate⁵⁻⁸. To enhance the spillover of CO from Ag sites to the Cu surface, various Cu-Ag nanostructure synthesis method was employed to enrich the boundary density between Cu and Ag⁹⁻¹³. More interesting, even though Cu and Ag are highly immiscible metals, due to the Gibbs free energy change contributed by the large surface area of the nanostructures, the alloying of Cu and Ag seems to be possible. Multiple ways have been developed in order to induce Ag atom into the Cu phase, including galvanic replacement¹⁴, co-sputtering¹⁵, ligands assisted co-deposition¹⁶, reoxidation/reduction-driven atomic interdiffusion¹⁷, and thermal shocking¹⁸. Although the rich chemistry of Cu and Ag at the nanoscale makes the further optimization of the CO₂ reduction process becomes feasible, the structural evolution of Cu-Ag bimetallic catalyst during the reaction is still largely underexplored, which leaves questions about the real catalytic sites and stability of the Cu-Ag bimetallic nanocatalysts.

Herein, in order to explore the structure and phase evolution of Cu-Ag bimetallic nanocatalysts under electrochemical CO₂RR, we prepared a highly uniform Cu-Ag nano-alloy through the thermal shock method. Due to the rapid heating and quenching process, this nano-alloy is stable for system characterization but also sensitive under electrochemical conditions. It turned out that even though prepared by the thermal shock method, the Cu-Ag nano-alloy catalyst cannot really form a single phase. Rather, the nanoparticles are composed of a Ag-doped Cu phase and a Cu-doped Ag phase. Activated by the CO₂ electroreduction condition, time-sequential high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) energy dispersive spectroscopy (EDS) mapping revealed the Cu can gradually leach out from the Cu-Ag nano-alloy and form a core-shell structure. Further prolonging the electrolysis time can make the segregation of Cu- and Ag-rich grains. Besides, the Cu content in Cu-rich and Ag-rich grains gradually disproportionated and approached the thermodynamic value¹⁹ during the electrolysis process. Cu-Ag nano-dimer can be obtained by thermal treatment of Cu-Ag nano-alloy. In contrast, although Cu-Ag nano-dimer also goes through structural evolution during CO₂ electrolysis, the elemental composition remains unchanged. To verify whether the evolution process of Cu-Ag nano-alloy surface is the same as the bulk result obtained above, Pb underpotential deposition (Pb-UPD) was developed. A very similar phase separation process was observed in Pb-UPD, confirms both bulk and surface of Cu-Ag nano-alloy are tends to form thermodynamically stable phases under electrochemical conditions. Furthermore, *Operando* high-energy resolution X-ray absorption spectroscopy (XAS) was then applied to confirm the Cu chemical states during electrolysis. It turned out the steady-state of Cu in the nano-alloy catalyst during CO₂RR is Cu(0). Interestingly, an anti-oxidation feature of this bimetallic catalyst was also observed.

3.2 Experimental method

Materials: Deuterium oxide (D₂O, 99.9 atom % D), potassium bicarbonate (KHCO₃, ACS reagent, 99.7%), dimethyl sulfoxide (DMSO, ACS reagent, ≥99.9%), Commercial Cu foil (thickness 0.25 mm, 99.98% trace metals basis), perchloric acid (HClO₄, 70%, 99.999% trace metals basis), sodium perchlorate monohydrate (NaClO₄·H₂O, ACS reagent), lead acetate trihydrate (Pb(OAc)₂·3H₂O, ACS reagent, ≥99%), silver nitrate (AgNO₃, 99.9999% trace metals basis) and copper(II) nitrate hydrate (Cu(NO₃)₂·xH₂O, 99.999% trace metals basis) were purchased from Sigma-Aldrich. Sodium chloride (NaCl, ACS, 99.0%), Commercial Ag foil (thickness 0.28 mm, 99.9% trace metals basis) and Platinum gauze (99.9% metal basis) were ordered from Alfa Aesar. Ag/AgCl (3M KCl) reference electrodes were purchased from CH Instrument and World Precision Instruments. Carbon dioxide (CO₂, 4.5LS), and Argon gas were purchased from Praxair. Deionized water (DI water with 18.2 MΩ·cm, <5 ppb TOC) was obtained from a Millipore water system. Carbon paper (Sigracet 29 AA) and Fumasep anion exchange membrane were ordered from Fuel Cell Store. The microwave oven (Panasonic Microwave Oven NN-SN686S, 1200W) was purchased from amazon.

Electrode preparations: The phased blended CuAg bimetallic catalyst electrodes were prepared based on the thermal shock method reported by the previous literature²⁰. Specifically, 1.167 mmol of CuNO₃ and 1.167 mmol of AgNO₃ salts were dissolved in 25 μ L of absolute ethanol solution and then dropped cast on the Sigracet 29 AA carbon paper on an area of 1 cm². After the ethanol evaporated, the carbon paper was sealed into an Ar saturated vial and irradiated by microwave for 10 s to quickly decompose the metal salt and generate CuAg bimetal nanoparticles. The prepared electrodes were then transferred into a vacuum desiccator for future uses.

To transform phased blended CuAg into CuAg dimers, the as-synthesized phased blended CuAg bimetallic catalyst electrodes were put into a tube furnace and annealed at 500 °C for 12 h under the Ar protection. After annealing, the synthesized CuAg dimers electrodes were also put into a vacuum desiccator for future uses.

Characterizations: Scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy (EDS), high-resolution transmission electron microscopy, and electron diffraction characterization of the catalysts were performed on a Thermo Fisher Scientific Titan 60-300 transmission electron microscope at an acceleration voltage of 300 kV. The electron microscope is equipped with four silicon drift EDS detectors with a total solid angle of 0.7 steradians. The L α peaks of Ag and the K α peaks of Cu in the EDS spectra were used for elemental mapping and composition quantification. The atomic compositions were calculated using the standardless Cliff-Lorimer correction method. Each EDS map was built based on the accumulation of 150 frames with a pixel dwell time of 8 μ s. Bruker Esprit software was used for the background subtraction of the EDS maps. X-ray diffraction (XRD) was measured by a Bruker D2 Phaser Diffractometer equipped with a Cu K α source. For all time-dependent electrolysis samples, electrodes were taken after CO₂ electrolysis under -1.0 V vs RHE for a certain amount of time, then rinsed with deionized water and ethanol repeatedly to remove electrolyte residues and dried in a vacuum desiccator.

The design of customized cell can be found in the previous reports²¹. Carbon paper was tailored into 1 $\times$ 5 cm² pieces as the catalyst support. The Cu NP catalysts were drop-cast on both sides of one end of the carbon paper (1 $\times$ 1 cm²) and the rest, 1 $\times$ 4 cm², served as a non-active conductor with negligible effects on the catalytic current, compared with the Cu-Ag electrocatalysts. The electrochemical cell consists of two pieces of chemically inert polyether ether ketone (PEEK) with an X-ray window in the middle (diameter = 1 mm) (Figure 3.11). One side of the PEEK has a shallow opening to maximize the collection of inherently weak HERFD signals only from the Cu K α_1 emission line (8048 eV), which was selected by Si single crystals ({444}), at an angle of 45° using a fluorescence detector. It enables a significantly enhanced energy resolution on the order of 1 eV, relative to the typical 50-200 eV of conventional solid-state fluorescence detector (e.g. Vortex). A Teflon U-shaped sealing ring was placed between the two PEEK pieces to adjust the electrolyte thickness to less than 200 μ m. On top of the electrochemical cell, a PEEK cap with one gas inlet and one gas outlet was used to bubble CO₂ gas in 0.1 M HCO₃. A carbon rod as the counter electrode (CE) was placed 3

cm away from the working electrode to avoid possible interference of electrochemical reactions on the CE on the WE. The reference electrode (Ag/AgCl (sat. KCl)) was placed (via a salt bridge) at the bottom of the cell to minimize the iR drop during electrochemical testing. All three electrodes were connected to a potentiostat (Biologic SP-200) during *operando* X-ray data acquisition. Cu K-edge XANES and EXAFS were acquired under HERFD mode at the PIPOXS beamline of the Cornell High Energy Synchrotron Source (CHESS). Cu K edge was calibrated based on the characteristic absorption edge of Cu metal foil at 8979.0 eV. Fourier transformed EXAFS spectra were plotted by applying a Hanning window from 3 to 10 $\text{\AA}^{-1}$ with k^2 -weighting and no phase correction.

Electrochemical test: The Biologic VSP-300 potentiostat was used for all electrochemical tests without further notation. Electrochemical tests were conducted in conventional H-cells. For all the CO₂RR experiments, the cathode and anode of the H cell were separated by an anion exchange membrane. The volume of the chambers is 50ml. 0.1 M KHCO₃ was used as the electrolyte. Before electrolysis, the electrolyte was firstly bubbled with CO₂ for at least 20 min to remove dissolved oxygen. The gas flow rate during electrolysis was controlled at 20ml/min by a mass flow controller at room temperature. Ag/AgCl (3M KCl) was used as the reference electrode.

Catalytic performances were tested with 85% IR compensated chronoamperometry (CA). The leftover 15% IR drop was manually compensated during the data analysis. All gases eluting from the outlet were sampled with a gas-tight syringe during the electrolysis. Gas products, including CO, CH₄, C₂H₄, C₂H₆, and H₂ were detected and quantified using gas chromatography (Agilent 7890B GC system). Liquid products were quantified by Bruker AV600 nuclear magnetic resonance (NMR) with water suppression technique. DMSO was utilized as the internal standard.

Lead underpotential deposition was performed in a three-necked flask with a carbon paper as the counter electrode and a Ag/AgCl (3M KCl) electrode as the reference electrode. Cyclic voltammetry (CV) curves were collected after the solution (0.1M NaClO₄, 3mM Pb(OAc)₂, 1mM NaCl, and acidified to pH 3 with HClO₄) was fully deoxygenated with Ar flow for 30 min. The scan rate was set as 5 mV/s.

3.3 Structural characterization of thermal shock synthesized Cu-Ag nanoparticles

As shown in Figure 3.1a, Cu-Ag bimetallic particles with tens of nanometer sizes were synthesized by the microwave thermal shock method. Based on EDS mapping, it can be found that Cu and Ag uniformly distribute from particle to particle regardless of the particle size. However, within a single particle, some Cu-rich and Ag-rich grains can be found with a size less the 10 nm (Figure 3.2).

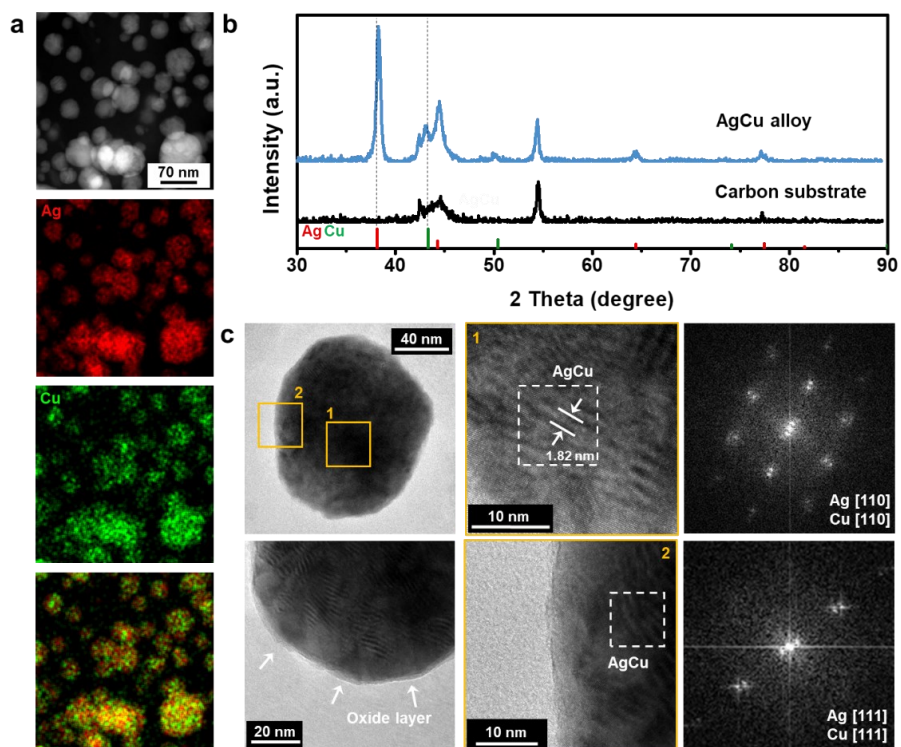


Figure 3.1. Structure characterization of the as-synthesized Cu-Ag nano-alloy. (a) HADDF-STEM EDS mapping and (b) XRD of the as-synthesized Cu-Ag nano-alloy. (c) TEM of the Cu-Ag nano-alloy, HRTEM and FFT of the selected area 1 and 2.

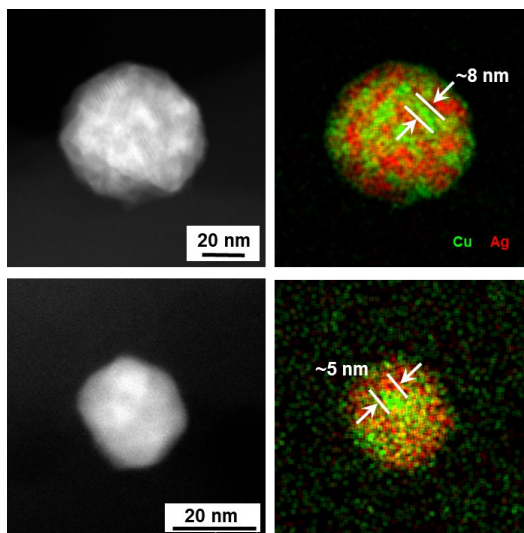


Figure 3.2. HADDF-STEM EDS mapping of as-synthesized Cu-Ag nano-alloy under larger magnitude to verify the phase blended feature and grain sizes.

EDS focuses more on local structure information while X-ray diffraction gives global structure information of Cu-Ag nano-alloy (Figure 3.1b). Importantly, two sets of diffraction peaks can be found, which are supposed to be assigned to Ag and Cu phases correspondingly. The observation of these two sets of peaks indicates that the as-synthesized Cu-Ag nano-alloy is indeed not a single-phase alloy. This is consistent with what we observed in EDS mapping. However, the diffraction peaks of Cu and Ag in the nanoalloys are shifted as compared with the standard diffractogram of monometallic Cu and Ag, indicating that the Cu and Ag phases are inter-doped.

High-resolution transmission electron microscopy (HRTEM) was also utilized to further confirm the structure information of the synthesized Cu-Ag nano-alloy (Fig 3.1c). A moiré pattern is observed in some images because of the coherent lattice orientation of the Ag-rich and Cu-rich grains, which was verified by a fast Fourier transform of the selected image area. Meanwhile, a ~2 nm thin oxide layer can be frequently found on the nano-alloy surface, which may be attributed to the exposure to the air during the transfer process.

3.4 Structural evolution of Cu-Ag nano-alloy under electrochemical CO₂RR

The electrochemical CO₂RR was performed on the as-synthesized Cu-Ag nano-alloy. Since it has been widely reported that the evolution of Cu under electrochemical conditions is strongly correlated to the applied potential and binding intermediates²²⁻²⁴, we choose a moderate potential as a representative condition on which the faraday efficiency (FE) toward hydrogen evolution reaction (HER) and CO₂RR is roughly half to half (Figure 3.3). Because the preparation of the HADDF-STEM EDS mapping sample is destructive to the electrode, we perform the CO₂RR electrolysis with different time durations on 6 Cu-Ag nano-alloy electrodes. A consistent structural evolution trend can be observed on Cu-Ag nano-alloy (Figure 3.4a). After 30min electrolysis, the enrichment of Cu on the nanoparticle surface can already be confirmed. A clear core-shell structure was then formed after 3h electrolysis. When electrolysis was further prolonged to 24h, some Cu was migrated from the nanoparticle surface and formed some segregated grains while others still stick to Ag grains.

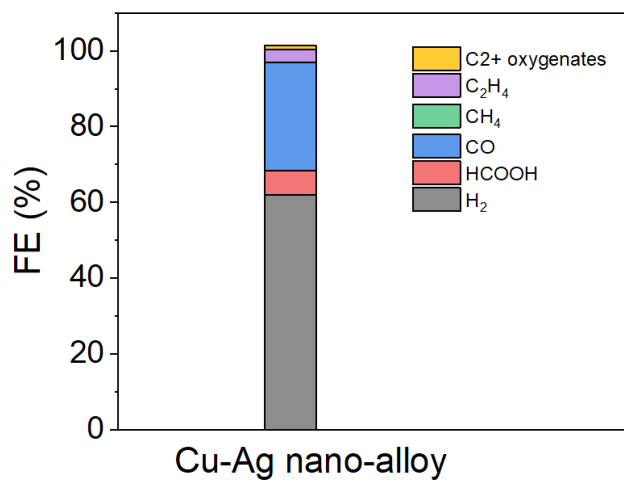


Figure 3.3. FE of the Cu-Ag nano-alloy catalyzed CO₂RR under -1.0 V s RHE.

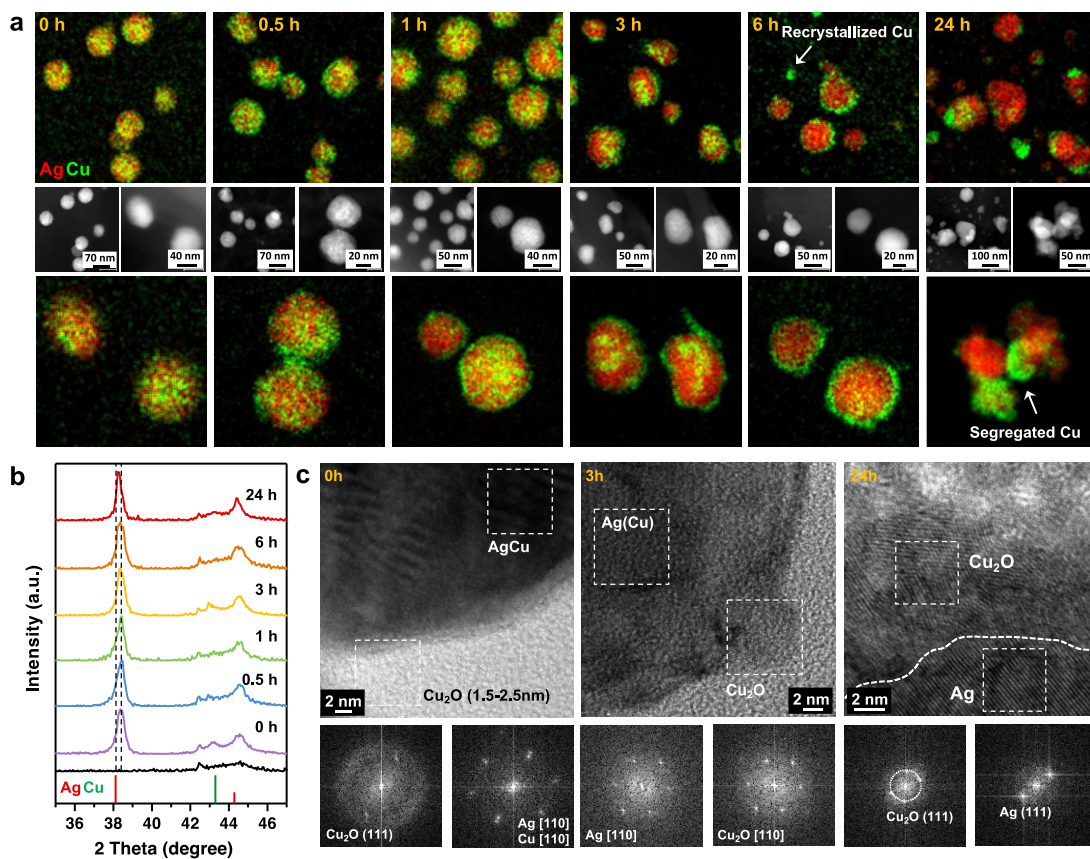


Figure 3.4. *ex situ* characterization of the evolution of Cu-Ag nano-alloy after 0 h, 0.5 h, 1 h, 3 h, 6 h, 24 h CO₂RR. (a) HADDF-STEM image and EDS mapping of the Cu-Ag nano-alloy structural evolution. (b) XRD patterns of Cu-Ag nano-alloy after CO₂RR for a

certain amount of time. (c) HRTEM and selected area FFT image of the Cu-Ag nano-alloy after 0h, 3h and 24h CO₂RR also exhibit a significant trend of Cu leaching out.

This continuous change is also reflected in the XRD spectrum (Figure 3.4b). It can be observed that the peak position of Ag (111) obviously shifts to lower angles after the electrolysis. However, even after 24h electrolysis, the Ag (111) peak in Cu-Ag nano alloy is still higher than in the standard spectrum, which indicates there is still a certain amount of Cu doped in the Ag grains.

Notably, the leached Cu-rich grains on the Cu-Ag nano-alloy catalysts were oxidized to Cu₂O when the grain size is relatively small. As shown in Figure 3.4c, the thickness of the oxide layer of as-synthesized Cu-Ag nano-alloy is limited to ~2 nm over the surface. After electrolysis, Cu₂O grains and shells of thickness between 2-8 nm were formed on the catalysts. It should be noted that the majority of Cu was recrystallized as separate particles with a size variation between 10-100 nm, or as large-size domains directly bound to the original catalyst. It is notable that SAED and EXAFS results corroborate that these Cu species mainly maintain a metallic state.

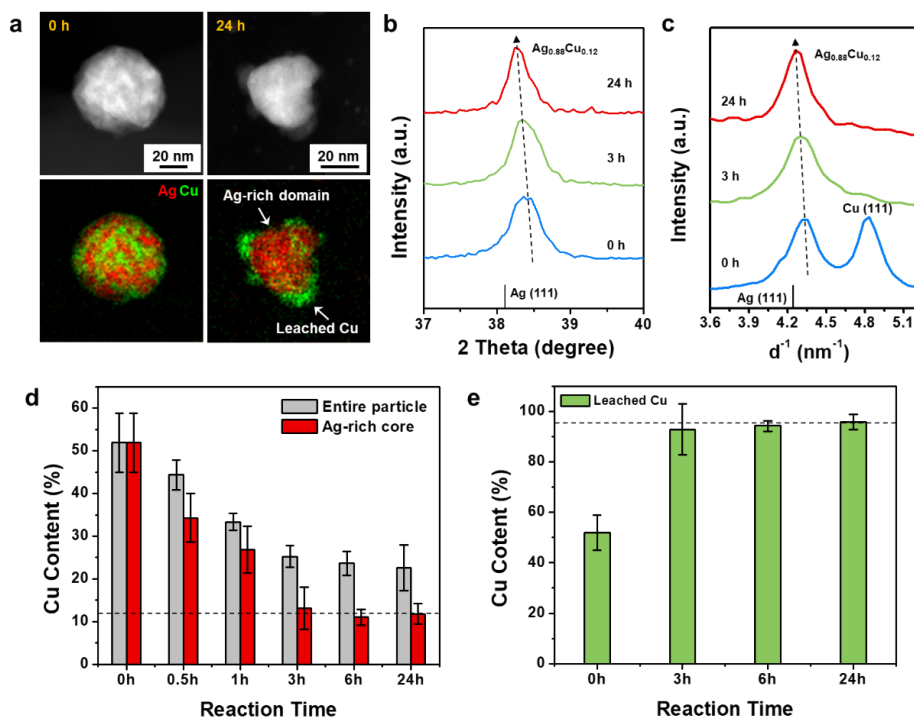


Figure 3.5. The trend of the evolution of Cu-Ag nano-alloy within 24 h CO₂RR. (a) HADDF-STEM and EDS mapping of the Cu-Ag nano-alloy before and after 24h CO₂RR. (b) XRD pattern and d-spacing of Ag (111) extracted from electron diffraction. (c) Time-dependent Cu contents in entire particles and Ag-rich cores. (d) Time-dependent Cu

contents in leached Cu grains. Data points with error bars (1 SD) in all figures are based on the average value extracted from at least 30 separate particles.

Further quantification was conducted to precisely describe the structural evolution of Cu-Ag nano-alloy during the CO₂ electrolysis (Figure 3.5a). Besides the XRD patterns in Figure 3.4b, the d-spacing of Ag (111) planes extracted from the electron diffraction during the electrolysis was also compared (Figure 3.5b), which exhibits an identical trend to XRD and further solidifies the conclusion we made. The Cu contents in entire particle, Ag- and Cu-rich grains are quantified through the EDS mapping spectrum, respectively (Figure 3.5c and d). The continuous decrease of the Cu content in the entire particle during the electrolysis indicates the leach out of the Cu. The Cu content difference of the entire particles before and after 24h CO₂ electrolysis cannot be explained by the dissolution of Cu into the electrolyte considering the pretty low solubility of Cu in the neutral CO₂RR condition. Therefore, this part of Cu is supposed to migrate from the nanoparticle surface to the substrate during the electrolysis and then agglomerate together to form copper-rich particles^{22, 25}. The Cu content in Ag-rich grains decrease as well and reached a steady state of 12% after ~3h electrolysis. Under the same time duration, the Cu content in the leached Cu grains increases to 95%. That is, after 3h electrolysis, the Cu-Ag nano-alloy is fully transformed from a metastable state to a more stable Cu- and Ag-rich phases, which can be denoted as Cu_{0.95}Ag_{0.05} and Cu_{0.12}Ag_{0.88}, respectively.

To verify whether the observed Cu_{0.95}Ag_{0.05} and Cu_{0.12}Ag_{0.88} are the thermodynamic stable phase, we transformed Cu-Ag nano-alloy into Cu-Ag nano-dimer with thermal treatment (Figure 3.6a). The Cu content in the Cu-Ag nano-dimer is strictly the same as what we quantified from the post 3h electrolysis Cu-Ag nano-alloy sample (Figure 3.6b). Further conducted electrolysis on this Cu-Ag nano-dimer sample will not further change its elemental composition. Meanwhile, no peak shift of Ag (111) can be observed in the XRD spectrum after electrolysis as well. (Figure 3.6c).

Notably, not only the elemental composition but also the morphology and surface structure of nanoparticles are important to the catalytic process. Therefore, although the evolution study of the Cu-Ag nano-alloy composition change provides important insights into the CO₂ electrolysis, more comprehensive characterizations are still indispensable for an in-depth understanding of this bimetallic catalytic system.

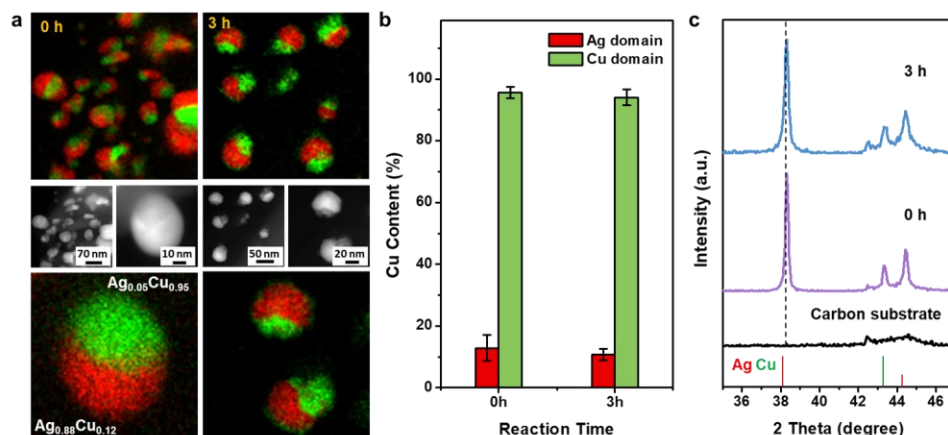


Figure 3.6. *ex situ* characterization of the evolution of the Cu-Ag nano-dimer before and after 3h CO_2RR . (a) HADDF-STEM image and EDS mapping of the Cu-Ag nanodimers structural evolution. (b) Quantified Cu content extracted from EDS mapping in Cu- and Ag-rich grains. (c) XRD patterns of the Cu-Ag nano-dimer before and after 3h CO_2RR . Data points with error bars (1 SD) in all figures are based on the average value extracted from at least 30 separate particles.

3.5 Surface evolution of Cu-Ag nano-alloy triggered by Pb-UPD

Since the electrocatalysis indeed happens on the catalyst-electrolyte interface, the surface structure, rather than the bulk, more directly influences the catalytic results and its importance cannot be ignored. Recently, more and more technologies have been built up to deepen our understanding of the surface chemistry in electrocatalysis²⁶⁻²⁹. Among the various surface characterization technologies, electrochemical methods exhibit their unique advantage by directly acting on the electrode surface and therefore sensitive to the local chemical environment. For example, H-underpotential deposition has become a classic method to probe the surface area and active sites of Pt-based catalyst³⁰⁻³¹ and the redox peak of Ir can be a method to quantify the Ir content in typical oxygen evolution catalysts³². However, the electrochemical characterization of Cu surfaces is more challenging for various reasons. Although double-layer capacitance can be used to quantify the Cu foil or Cu mesh electrochemical surface area (ECSA), it is not applicable for the carbon substrate supported Cu nanoparticles due to the huge capacitance contribution from the substrate. Meanwhile, Cu is a non-noble metal and pretty dynamic. During the redox cycles, the severe surface or even the bulk structural evolution will make the surface characterization meaningless. Some researchers use the OH^- adsorption peak to identify the Cu surface structure³³ but these characteristic peaks are also partially overlapped with the Cu oxidation peak, leading the irreversible surface reconstruction.

Recently, Pb underpotential deposition (Pb-UPD) has been utilized to characterize Cu surface structure which is sensitive and not influenced by the carbon substrate³⁴⁻³⁵. Therefore, the surface structure of Cu-Ag nano-alloy can be further probed via this

method. The commercial Cu and Ag foil were utilized as two references in Pb-UPD experiments, which exhibits the Pb stripping peak at -0.254 V and -0.284 V vs 3M Ag/AgCl reference electrode (Figure 3.7). Interestingly, a major peak located at -0.303 V and a tiny peak located at -0.226 V vs 3M Ag/AgCl can be found in the first CV cycle of the Cu-Ag nano-alloy, which might be attributed to the Pb stripping on the alloy phases and the defected Cu sites³⁴. Different from Cu and Ag foil, which is stable under Pb-UPD conditions, the Pb stripping peaks of the Cu-Ag nano-alloy evolves quickly ((Figure 3.8). It could be found that the pristine -0.303 V vs 3M Ag/AgCl peak gradually decrease and separated into two peaks which can fit well with the peak positions of Cu and Ag foil. This indicates that during the electrochemical condition, the surface of the Cu-Ag nano-alloy also goes through phase separation and results in the Cu- and Ag-dominated phase. Since the Pb stripping peak only reflects the binding strength between the metal surface and Pb atom, it is still arguable whether the surface is pure Cu and Ag phase or the trace metal inter-doped phase does not significantly influence the binding affinity. However, considering the inter-doped phase shows a Pb stripping peak shift in the Cu-Ag nano-dimer (Figure 3.9), we prefer to believe that there is no mutual interference between Cu and Ag domains on the nano-alloy surface after the phase separation. Although the extent may vary, our Pb-UPD experiments confirm that both bulk and surface of Cu-Ag nano-alloy go through an electrochemically triggered phase separation process. On the other hand, the tiny defected Cu peak located at -0.226 V vs 3M Ag/AgCl becomes larger in the first few CV cycle and then disappear, which can be correlated to the Cu leaching out and aggeneration, correspondingly.

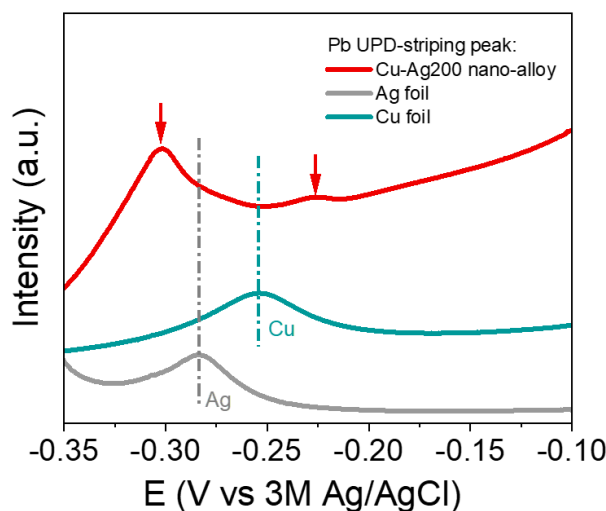


Figure 3.7. Pb stripping peaks of the Cu-Ag nano-alloy in Pb-UPD experiment. The first cycle was plotted in order to avoid the surface reconstruction of the Cu-Ag nano-alloy. Pb stripping peaks of Cu foil and Ag foil were included for comparison.

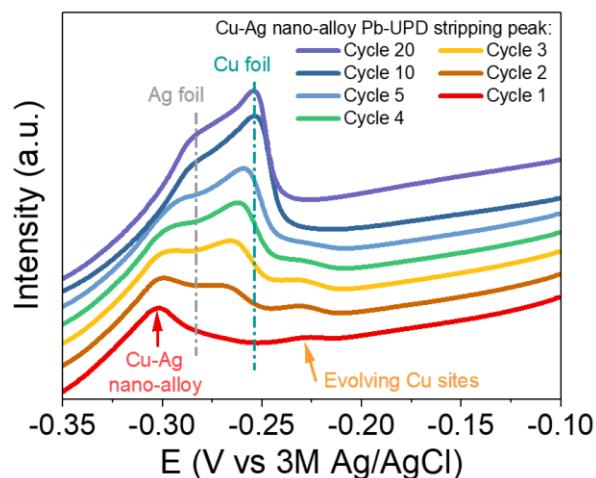


Figure 3.8. Sequential Pb stripping peaks of the Cu-Ag nano-alloy in Pb-UPD experiment. In the Pb-UPD experiment, Pb was deposited on Cu-Ag nano-alloy during the cathodic scan and stripped in the anodic scan. 20 cyclic voltammetry cycles were recorded to track the surface evolution of the Cu-Ag nano-alloy.

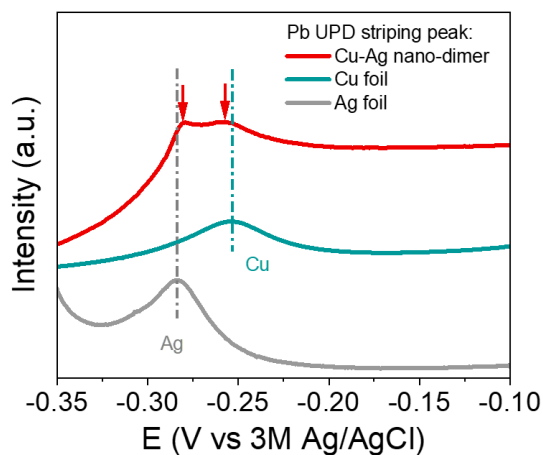


Figure 3.9. Pb stripping peaks of the Cu-Ag nano-dimer in Pb-UPD experiment. The first cycle was plotted in order to avoid the surface reconstruction of the Cu-Ag nano-dimer. Pb stripping peaks of Cu foil and Ag foil were included for comparison.

3.6 *Operando* high-energy-resolution XAS studies of Cu-Ag alloy electrocatalysts

We employed *operando* high-energy resolution fluorescence detector (HERFD) X-ray absorption spectroscopy (XAS) to investigate the electronic structure and coordination

environment of Cu-Ag alloy electrocatalysts under real-time reaction conditions and assess the role of Ag in suppressing Cu oxidation. The HERFD detector selects the Cu $K\alpha_1$ emission line as one particular fluorescence decay channel, which significantly extends the core hole lifetime³⁶⁻³⁷. Thus, the HERFD XAS can allow a much higher energy resolution on the order of 1 eV, given the energy-time uncertainty principle, when compared to a conventional X-ray fluorescence detector (50-200 eV)³⁸⁻⁴⁰. HERFD X-ray absorption near-edge structure (XANES) spectroscopy resolves the pre-edge peaks of Cu, Cu₂O, and CuO reference samples, which are significantly better than conventional XANES spectra, as exemplified by the notable identification of the pre-peak of CuO at ~8977 eV originating from the Jahn-Teller distortion of [Ar]3d⁹ configuration (Figure 3.10). Cu₂O shows the characteristic pre-edge peak at 8981.0 eV with a 1.2 eV positive shift, relative to Cu (8979.8 eV). The homemade HERFD XAS electrochemical cell²¹ is capable to deliver comparable electrochemical results of Cu-Ag alloy electrocatalysts to a standard H-cell and a well-defined current plateau under the CO₂RR condition (Figures 3.11 and 3.12).

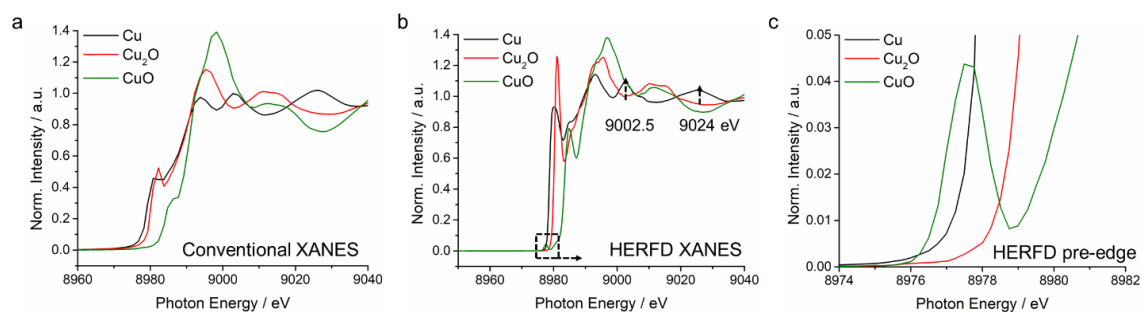


Figure 3.10. (a) XANES spectra of standard references of Cu foil, Cu₂O and CuO powders were collected with a conventional solid-state fluorescence detector. (b) High-energy-resolution XANES spectra of the same reference samples, using the HERFD detector, show much better-resolved pre-edges at around 8980 eV. Dashed arrows indicate the intensity increase at 9002.5 and 9024 eV from Cu₂O to metallic Cu. (c) The enlarged region from the dashed box in (b) clearly shows the pre-peak of CuO at 8977.6 eV due to the Jahn-Teller distortion, which was not resolvable in conventional XANES spectra.

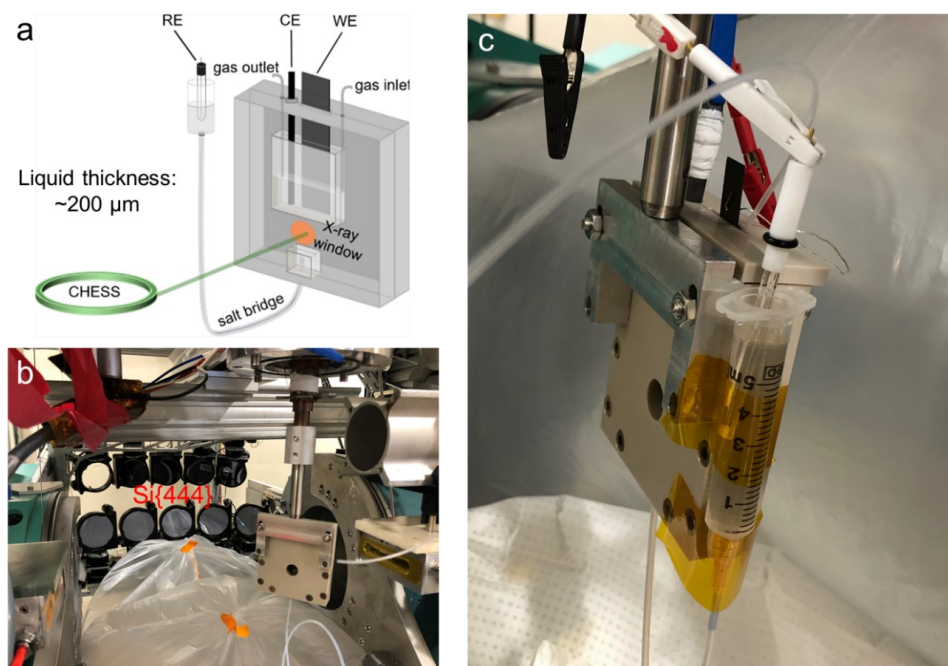


Figure 3.11. *Operando* HERFD XAS setup. (a) Schematic of the XAS electrochemical cell with the working electrode (WE, Cu-Ag alloy NPs synthesized on carbon paper) and counter electrode (CE, carbon rod) immersed in CO₂-sat. 0.1 M KHCO₃. The reference electrode (Ag/AgCl in sat. KCl) was connected to the cell by a salt bridge to minimize the IR drops caused by the resistance in the thin liquid layer (<200 μm) within the X-ray window. (b-c) Photos of the XAS cell operating at CHES with five pairs of Si{444} single crystals to select Cu Kα₁ emission line for HERFD analysis with a high energy resolution of ~1 eV.

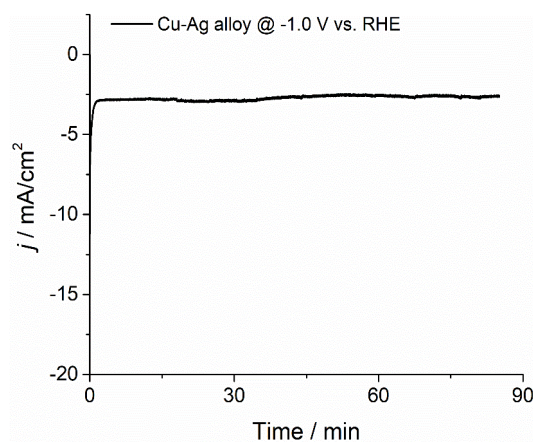


Figure 3.12. Stable operation of Cu-Ag alloy electrode at -1.0 V vs. RHE in CO₂-saturated 0.1 M KHCO₃ using operando HERFD X-ray cell.

Operando XANES of Cu-Ag alloy electrocatalysts were performed during the CO₂RR (Figure 3.13a). XANES spectrum of pristine Cu-Ag alloys presents the co-existence of metallic Cu and Cu₂O, when compared to standard references (Figure 3.13b, dashed lines). At -1.0 V vs. RHE, XANES pre-edge peaks at around 8979 eV show the progressive negative shifts, particularly after 40 min, corresponding to the electroreduction of Cu₂O to metallic Cu. In addition, post-edge peaks at 9002.5 and 9024 eV (dashed red arrows in Figure 3.13a) further support the conversion from Cu₂O to Cu under electroreduction (Figure 3.10b). Quantitative analysis using pre-edge peaks suggests that metallic Cu fraction increases from about 60% of the pristine Cu-Ag alloys to about 90% after 40 min and approaches nearly 100% after 80 min electroreduction (Figure 3.13a, inset and Figure 3.14). Corresponding extended X-ray absorption fine structure (EXAFS) spectra show the diminution of Cu-O bonding and the increasing contributions of Cu-Cu bonding (Figure 3.13d and Figure 3.15). Those *operando* X-ray studies suggest that metallic Cu is the active state for reducing CO₂ to multicarbon products.

One pressing challenge facing the development of Cu electrocatalysts is whether the re-oxidation (i.e. deactivation) of active metallic Cu sites³⁴ can be mitigated or minimized, so as to maintain active structures of electrocatalysts after the CO₂RR and enhance the catalyst durability in realistic applications. After three-week air exposure, we examined the *ex situ* XAS of Cu-Ag electrocatalysts (Figure 3.13c and d). Surprisingly, Cu-Ag alloys maintain the metallic features, as indicated by the horizontal dashed line in XANES spectra (Figure 3.13c). Examination of k²-weighted EXAFS spectra clearly shows that Cu-Ag alloy electrocatalysts experienced electroreduction from Cu₂O to metallic Cu (red dashed arrows) (Figure 3.13d). Upon long-time air exposure, Cu in Cu-Ag alloys maintains the metallic features, as evidenced by the lack of Cu-O bonding at 1.5 Å and the persistent existence of triplet metallic Cu features at ~4.5 Å. The amplitude of Cu-Cu bonding exhibits a noticeable decay upon air exposure (green dashed arrows), which is possibly due to the structural reconstruction, such as fracturing of large Cu domains, leading to lower coordination numbers and/or more disordered structures upon air exposure. Although the HRTEM image in section 3.4 shows a thin layer of the oxides on the nanoparticle surface, we note that this is not contradicting our observation in *Operando* HERFD XANES and EXAFS due to the relatively low signal response of Cu₂O compared with Cu. Our spectroscopy observation focuses more on the anti-oxidation property of the alloy phase rather than the phase-separated Cu grains. In summary, *Operando* HERFD XANES and EXAFS present unambiguous evidence to show that Cu in Cu-Ag alloys experiences the electroreduction of surface Cu₂O to metallic Cu as possible active sites for the CO₂RR, and Ag in the Cu-Ag alloy plays an instrumental role in suppressing Cu oxidation.

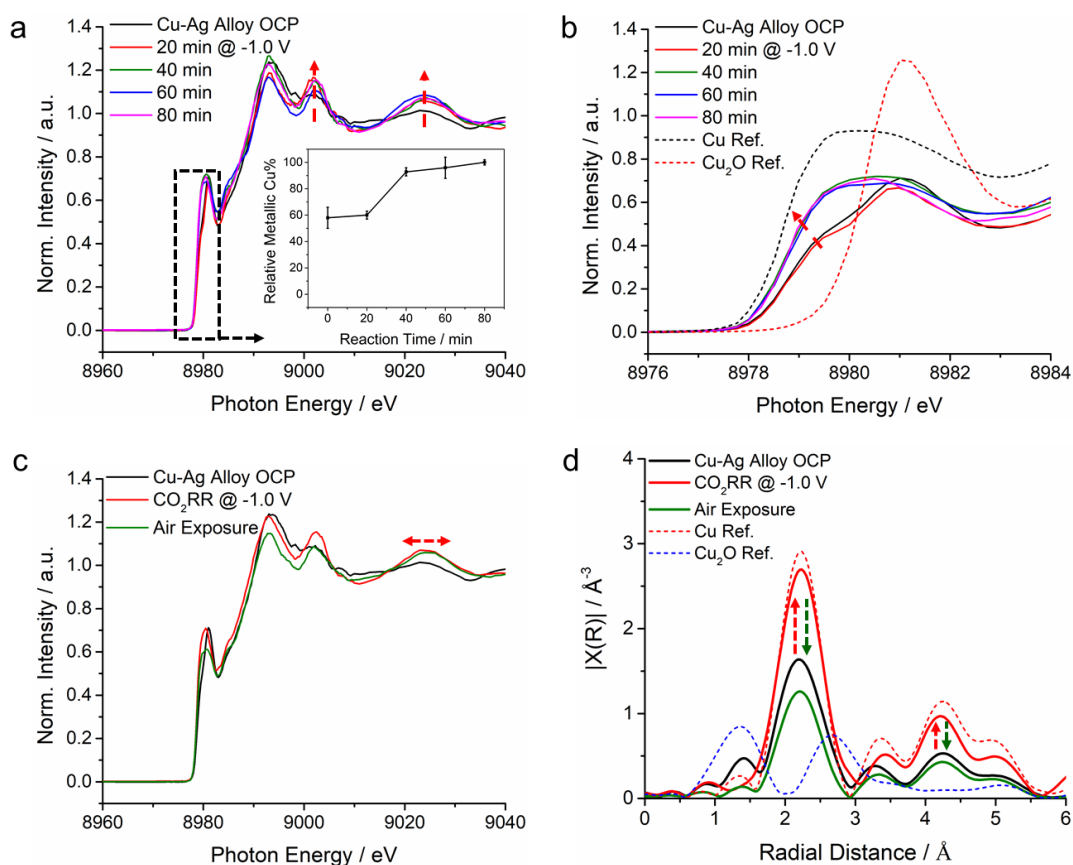


Figure 3.13. *Operando* HERFD XAS studies of valence states and coordination environments of Cu-Ag alloy electrocatalysts. (a) *Operando* HERFD XANES of Cu K-edge of Cu-Ag alloy as a function of reaction time at -1.0 V vs. RHE in CO₂-sat. 0.1 M KHCO₃. Insets show the quantitative analysis of relative metallic Cu fraction %. (b). XANES pre-edges of Cu-Ag alloy magnified from the dashed box region in (a) in comparison with Cu and Cu₂O references (dashed lines). (c-d) *Operando* XANES and corresponding EXAFS spectra of Cu-Ag before, during and upon air exposure after the CO₂RR.

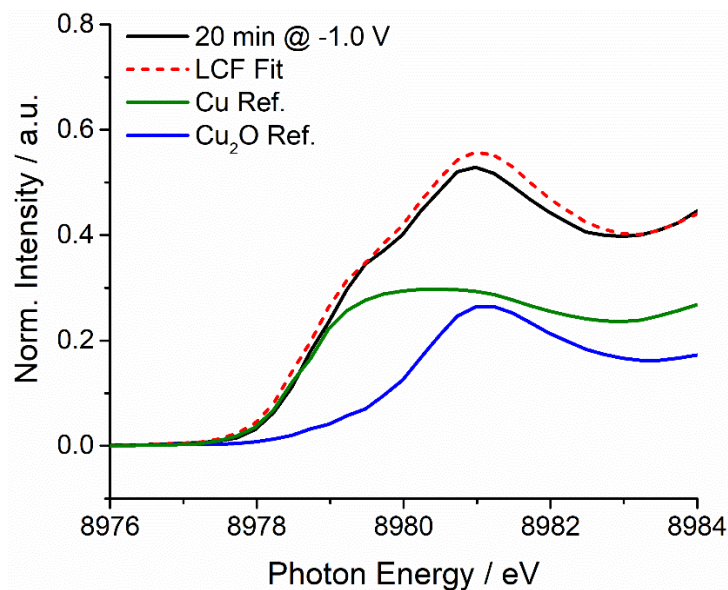


Figure 3.14. Example of Linear combination fitting (LCF) for HERFD pre-edge peak of Cu-Ag after 20 min CO₂RR at -1.0 V vs. RHE, resulting in the relative composition of 60% metallic Cu and 40% Cu₂O. The error bar was estimated to be around 3% with a reduced χ^2 of 0.00034. Note that the typical criterion of high-quality LCF is a reduced χ^2 value less than 0.001 (0.1%).

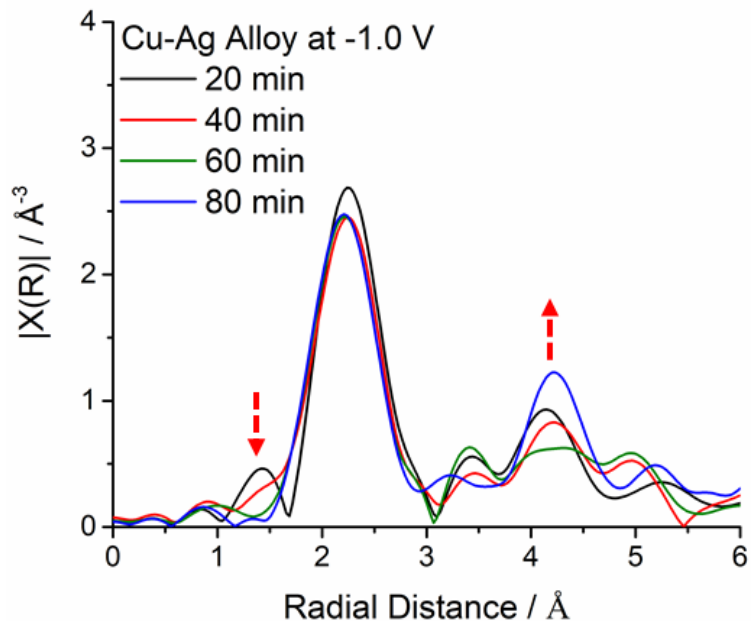


Figure 3.15. *Operando* time-resolved EXAFS of Cu-Ag alloy at -1.0 V vs. RHE with the dashed arrows pointing out the decrease of Cu-O feature and increases of metallic Cu feature.

3.7 Conclusion

In summary, this effort focuses on the exploration of the structural evolution of Cu-Ag bimetallic system in electrochemical CO₂RR conditions. We synthesized a 1:1 atomic ratio Cu-Ag nano-alloys by the microwave thermal shock method. Due to the thermodynamic prohibition, the Cu-Ag nano-alloy consists of sub-10nm Cu- and Ag-rich phases rather than a single intermetallic phase. Under the CO₂RR condition, the phase separation and the structural reconstruction of Cu-Ag nano-alloys were observed. Cu gradually leaches out, firstly forming a core-shell structure and then migrating and forming segregated grains. The final stable metal compositions in the Cu- and Ag-rich phase are Cu_{0.95}Ag_{0.05} and Cu_{0.12}Ag_{0.88}, respectively. Furthermore, the surface reconstruction was also explored with the Pb-UPD. It has been found that the surfaces of Cu-Ag nanoalloys undergo the same evolution process, but possibly to a different extent. Besides *ex situ* characterizations, *Operando* HERFD XANES and EXAFS were also applied to study the structural information of Cu-Ag nano-alloys under the electrochemical condition. It was more definitely confirmed that Cu(I) can be fully reduced to Cu(0) in the Cu-Ag system. Meanwhile, the after electrolysis anti-oxidative phenomenon of Cu in the Cu-Ag alloy was also found. In short, this work sheds light on the structure and phase evolution of Cu-Ag nano-alloys in CO₂RR and facilitates the understanding of the interactions between Cu and Ag, which is important in designing next-generation Cu-Ag bimetallic catalysts for efficient CO₂RR.

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Chapter 4 Bio-Inspired Asymmetric C-C Coupling in Tandem CO₂ Electroreduction

Parts of the content of this chapter were reprinted and adapted from the following work with permission: Chubai Chen, Sunmoon Yu, Yao Yang, Sheena Louisia, Inwhan Roh, Jianbo Jin, Shouping Chen, and Peidong Yang. “Bio-inspired asymmetric C-C coupling in tandem CO₂ electroreduction”, under review.

4.1 Introduction

Although a wide range of interests has been stimulated aiming to convert CO₂ into value-added multicarbon chemicals with more control over catalytic selectivity¹⁻⁴, as the principal step to constructing carbon skeletons, the C-C coupling mechanism in CO₂ fixation chemistry is not well understood and needs further investigations.

Interestingly, some bacteria in nature can digest CO₂ through the Wood–Ljungdahl metabolic pathway (W-L pathway) and efficiently transform them into acetate with unity selectivity. In the past decades, extensive research efforts have been made to reveal the underlying mechanisms of CO₂ transformation and C-C coupling in the W-L pathway and a molecular-level understanding has been established⁵⁻⁶. Concretely, CO₂ molecules are first converted into methyl groups and carbonyl groups in the western and eastern branches of this pathway. These two groups then go through asymmetric C-C coupling with the assistance of acetyl-CoA synthase, resulting in acetate production (Figure 4.1a).

For direct CO₂ electroreduction, copper (Cu) has attracted significant attention as a catalyst among many other inorganic materials since it is the only metal that can activate C-C coupling and therefore generate products beyond C1 chemistry (C₂H₄, C₂H₅OH, CH₃COOH, n-C₃H₇OH, etc.). However, due to its complexity of CO₂ reduction on the copper surface, understanding the coupling process on the Cu surface is still regarded as one of the central challenges in CO₂RR after decades of research^{1, 7}. Currently, it is widely accepted that carbon monoxide (CO) generated from CO₂RR is the key intermediate for symmetric C-C coupling⁸⁻⁹. One concrete experimental evidence is that the potential window and product spectrum of both CO reduction and CO₂ reduction shows a high degree of consistency¹⁰. Nevertheless, there is still a lack of a comprehensive and convincing molecular picture of such C-C coupling. While some DFT calculations and *in situ* spectroscopical evidence support the direct CO-CO dimerization on the Cu surface (*CO-*CO)¹¹⁻¹³, some other calculation results indicate that the protonation of *CO towards either hydroxymethylidyne (*COH) or formyl (*CHO) prior to C-C coupling is more thermodynamically favored under acidic to neutral pH¹⁴⁻¹⁶. Accordingly, *COH or *CHO would participate in the downstream C-C coupling. However, the exact role of these two intermediates is also debatable^{15, 17-19}. The lack of consensus can be attributed to several factors: the significant dependence of DFT results

on modeling and algorithms, the catalytic sensitivity towards applied potentials, surface pH, Cu active sites, electrolyte species, and surface modifiers within the double layer²⁰⁻²⁴.

Although the asymmetric coupling between *CO and *CHO (*COH) has been explored for CO₂RR, very few efforts go further to discuss the possibility of the Wood–Ljungdahl pathway-like *CH₃ and *CO coupling in inorganic aqueous CO₂ electrolysis. One important reason why the study of asymmetric coupling is hampered is the challenge in correlating the experimentally detected *CH_x (x=1-3) signals in the *operando* spectrum to any particular intermediates or process²⁵⁻²⁶. Recently, some studies hypothesized that the *CH_x-*CO asymmetric coupling may happen under a CO concentrated environment (either generated by tandem catalyst architecture²⁷⁻²⁸ or high-pressure CORR²⁹) and contribute to the final product selectivity. Nevertheless, without experimental evidence, it is still uncertain whether Cu has the ability to achieve asymmetric couplings on its surface during aqueous CO₂ electrolysis. The product spectrum of asymmetric coupling and the corresponding conversion mechanism is also unclear at this point (Figure 4.1b).

Here, we first designed co-reduction experiments to verify the catalytic capability of Cu surfaces for asymmetric *CH₃-*CO coupling by using an electropolished Cu foil (Figure 4.1c). In order to circumvent the dilemma that it is difficult to specify intermediates from the spectrum, we assure the existence of the intermediates by externally feeding the CO and CH₃I as the two distinct intermediate sources. While *CO comes from the adsorption of CO gas, *CH₃ is electrochemically generated from CH₃I. By further labeling CH₃I with ¹³C isotope, the verification of ¹³C-¹²C asymmetric coupling became technically feasible via nuclear magnetic resonance (NMR) spectroscopy. During the electrolysis of CH₃I, we found that a portion of the generated methyl group can be stabilized on the Cu surface even in a highly polar aqueous electrolyte. These methyl groups can then participate in the C-C coupling reaction and be coupled with another *CH₃ or *CO, generating several multicarbon products (C₂H₆, CH₃CHO, C₂H₅OH, CH₃COOH, (CH₃)₂CO) on the Cu surface. After the asymmetric coupling ability of Cu was confirmed, we moved to more practical CO₂ reduction electrocatalysis with a tandem Cu-Ag nanoparticle assembly (Figure 4.1c). Mimicking the Wood–Ljungdahl pathway, Cu is responsible for *CH_x intermediates generation and Ag is for most of the *CO in this tandem system. Since directly quantifying the concentration of the intermediates on the Cu surface is challenging, we utilized the production rates of CH₄ and CO as the intermediate spectators. The rate of CH₄ and CO can be tuned by changing the Cu-Ag ratio and the applied potentials. A maximum multicarbon oxygenates generation rate was achieved when CH₄ and CO production rate was aligned.

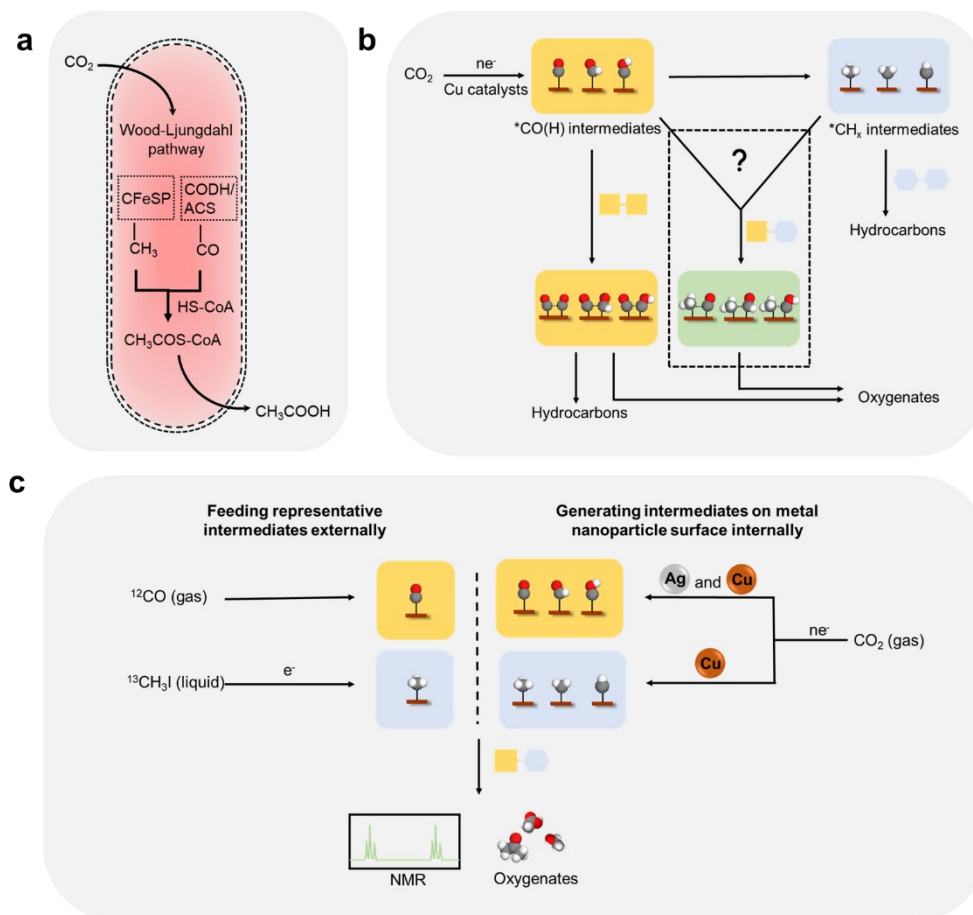


Figure 4.1. (a) Schematic illustration of *CH₃-*CO asymmetric coupling in the Wood-Ljungdahl pathway as a natural CO₂ bio-fixation process. (b) Schematic illustration of symmetric and underexplored asymmetric coupling process in inorganic CO₂ electroreduction. (c) In this effort, isotope labeled intermediates are externally fed to verify the existence of the asymmetric coupling process on a Cu surface. Afterward, Cu-Ag nanoparticle assembly is used to generate asymmetric coupling intermediates internally in CO₂ electroreduction, demonstrating the feasibility to mimic W-L pathway with inorganic catalysts.

4.2 Experimental method

Materials: Commercial Cu foil (thickness 0.25 mm, 99.98% trace metals basis), deuterium oxide (D₂O, 99.9 atom % D), methyl iodide (contains Cu wire as the stabilizer, 99.5%), o-phosphoric acid (85%, Supelco®), carbon rod (L150mm, Diam. 6mm, 99.995% trace metals basis), potassium bicarbonate (KHCO₃, ACS reagent, 99.7%), potassium carbonate (K₂CO₃, 99.995% trace metals basis), potassium hydroxide (KOH, 99.99% trace metals basis), dimethyl sulfoxide (DMSO, ACS reagent, ≥99.9%) and airbag (Supel™-Inert Multi-Layer Foil) were purchased from Sigma-Aldrich. Commercial Ag

foil (thickness 0.28 mm, 99.9% trace metals basis) and Platinum gauze (99.9% metal basis) were ordered from Alfa Aesar. Glassy carbon electrode (CHI104) and Ag/AgCl (3M KCl) reference electrodes were purchased from CH Instrument and World Precision Instruments. Glassy carbon plate (25 mm×25 mm) was purchased from SPI supplies, and glassy carbon planchet (Dia. 25 mm) was purchased from Ted Pella. Carbon monoxide (4.0 research), Carbon dioxide (CO₂, 4.5LS), and Argon gas were purchased from Praxair. Deionized water (DI water with 18.2 MΩ·cm, <5 ppb TOC) was obtained from a Millipore water system. Isotope labeled ¹³CH₃I (99%) was purchased from Cambridge Isotope Laboratories, Inc. Fumasep and Selemion AMV anion exchange membrane was ordered from Fuel Cell Store and AGC Engineering.

Electrode preparation: The electrochemical polish parameter in the previous report³⁰ was used here. Specifically, the as-received Cu foil was first cut to the desired size, then sonicated in an ethanol bath and DI water bath sequentially in order to remove the organic contamination on the Cu surface. Then the Cu foil was dipped into the 85% o-phosphoric acid and electrochemically polished with a carbon rod as the counter electrode. The electrochemical polish process would last for 10min under the applied potential of 2.1V vs carbon rod. After the electrochemical polish, Cu foil was rinsed with DI water to remove acid on the surface and then blow-dried with Ar flow. The prepared EC-Cu is then immediately used for the characterization of electrochemical tests.

For Cu and Ag nanoparticle synthesis, previously reported recipes were followed³¹⁻³³. NPs were spin-coated on the glassy carbon planchet, and this process was optimized to load NPs close to a monolayer. To form a tandem NP system, Cu and Ag NP solutions were mixed and spin-coated on the support by using a spin coater (Laurell WS-400A-6NPP/LITE). For instance, to make Cu50Ag50 where 50% of the total number of NPs was Cu NPs, the concentration of each Cu and Ag NP solution was taken into account when a mixed solution was prepared. The active area of the electrode exposed to the electrolyte was 1.13 cm².

Characterizations: The images of Cu surface morphology were acquired by using an FEI Quanta 3D FEG/FIB SEM with the operation condition of 5 kV and 3.4 nA. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha) characterization was conducted using an Al Kα source. In order to measure the post-electrolysis sample, EC-Cu foil was sampled after CH₃I and CO co-reduction under -0.8V vs RHE for 6h. The foil was then rinsed with deionized water to remove as much electrolyte residue as possible and blow-dried with Ar flow. Post electrolysis SEM images of the Cu-Ag nanoparticles were directly collected on the glassy carbon substrate after the CO₂RR is finished. For TEM based characterizations, nanoparticles were redispersed into the solvent by ultrasonication, then deposit on the TEM grids. Atomic-scale high-angle annular dark-field detector scanning transmission electron microscopy (HAADF-STEM) images and elemental electron energy loss spectroscopy (EELS) maps were acquired on a fifth-order aberration-corrected STEM (Cornell Nion UltraSTEM) operated at 100 keV with a beam convergence semi-angle of 30 mrad. Sub-Ångström spatial resolution is

achievable under such operating conditions. EELS spectral images were acquired with a 0.25 eV/channel energy dispersion (energy resolution, 1.0 eV) in a Gatan spectrometer with a size of 100 pixels and an acquisition time of 10 ms/pixel. EELS spectrum images were processed using principal component analysis (PCA, 3 components) and the linear combination of power law (LCPL) to subtract the background, in ImageJ software. In addition, the energy dispersive X-ray (EDX) mapping was acquired in STEM mode using the Titan Themis microscope at National Center for Electron Microscopy (NCEM) at LBNL. STEM-EDX maps were acquired for 30-40 min with drift correction using the Velox software and an estimated spatial resolution of 1-2 nm at 300 keV and about 0.6 nA beam current using a quadruple Bruker EDX detector with a large solid angle of 0.7 steradian. High-resolution bright-field TEM (HR-TEM) images were also acquired on Themis at 300 keV.

Electrochemical test: Electrochemical tests were conducted in conventional H-cells. For all the CH₃I and CO related experiments, the cathode and anode of the H cell were separated by an anion exchange membrane. The volume of electrolyte in both chambers was 50ml. Before electrolysis, the electrolyte was firstly bubbled with carrier gases for at least 20 min to remove dissolved oxygen. 0.1 M KHCO₃ was used as the default electrolyte other than the specific conditions stated in the manuscript. The gas flow rate during electrolysis was controlled at 10ml/min by a mass flow controller at room temperature. Ag/AgCl (3M KCl) was used as the reference electrode. For NP based CO₂RR experiments, the volume of the electrolyte in both chambers was 17 ml while the gas flow rate was 20 ml/min. Besides that, other operating conditions and procedures were identical.

In double-layer capacitance measurement, gas flow and stir bar were stopped after the system was fully deoxygenated. Meanwhile, the gas outlet was also sealed. The potential range of cyclic voltammetry (CV) scans was set from -0.1V to 0.25V vs RHE. Through linear regression, the slope of the charging and discharging currents with respect to the scan rates could be obtained, which correspond to the surface's double-layer capacitance.

The polarization response curves were also collected with CV technique. After the CV curve was stable (usually after 5 loops), the cathodic scan sections between 0.1V and -0.9V vs RHE were then collected and plotted for comparison. 10 μ l CH₃I was added to the electrolyte for the investigation of the characteristic reduction peak and operation window of CH₃IRR.

Catalytic performances were tested with 85% IR compensated chronoamperometry (CA). The leftover 15% IR drop was manually compensated during the data analysis. The deviation of actual potential from expected potential is normally smaller than 25mV, which is not supposed to influence any of the comparison or conclusions in this effort relative to the 200mV or 150 mV intervals applied in the electrochemical tests. For the co-reduction experiments, while the gas flow was kept constant during the 6h electrolysis, two doses of 50 μ l of CH₃I were added to the cathodic chamber at 0h and 3h, respectively. Because of the hazards associated with handling CH₃I (i.e., volatile and highly toxic), all CH₃I relevant operations need to be performed in a fume hood accordingly. During each

3h electrolysis period, the current gradually decreased due to the consumption of CH₃I reduction as well as CH₃I evaporation with gas flow. All gases eluting from the outlet were cumulated in a gas bag during the electrolysis in order to obtain an averaged result. Liquid products were sampled after 6h electrolysis. For CO reduction reaction without CH₃I, gas can directly be sampled from headspace with a syringe, and a gas bag is no longer necessary.

Products analysis: After electrolysis, gas products, including CO, CH₄, C₂H₄, C₂H₆, and H₂ were detected and quantified using gas chromatography (Agilent 7890B GC system). An additional 10min baking at 200°C was added into the GC program to remove the CH₃I vapor trapped in the column. For nanoparticle based CO₂ electrolysis, gas products were measured by gas chromatography (SRI MG3) equipped with a thermal conductivity detector and a flame ionization detector. Liquid products were analyzed by 1H nuclear magnetic resonance spectroscopy (Bruker AV600 with a 5 mm Z-gradient triple resonance 1H/BB Prodigy cryo-probe) with water suppression by excitation sculpting. 900μl aliquot and 100μl DMSO-D₂O solution were mixed for locking purposes, in which DMSO was used as the internal standard for quantification.

4.3 CH₃I and CO reduction on electrochemically polished Cu foil

4.3.1 CH₃I chemical behavior on Cu under reductive potentials

Electrochemically polished Cu foil (EC-Cu) was chosen as a model Cu catalyst for the co-reduction experiments. The representative surface morphology of Cu foil before and after electrochemical polish (Figure 4.2a and b) was characterized by a scanning electron microscope (SEM). It was found that most of the rough features on the pristine Cu foil disappeared after the polish, giving a smoother surface. Meanwhile, double-layer capacitance measurement showed that the specific capacitance of EC-Cu decreased from 187.8 μF/cm² to 54.3 μF/cm² (Figure 4.2c), which is a typical value for the EC-Cu and is consistent with the previous reports³⁴. Elemental information of EC-Cu was also collected through X-ray photoelectron spectroscopy (XPS) to track the potential contamination after electrolysis (Figure 4.3). The only increased signals can be attributed to the surface absorbed iodine stemming from the electrolysis of CH₃I. However, this trace amount of surface contamination detected here should not significantly affect our designed experiments.

Alkyl halides are widely used as alkylating reagents in organic³⁵ and electro-organic³⁶ synthesis. Specifically, CH₃I was selected as the methyl providing reagent in this effort, considering the solubility of CH₃I in aqueous electrolyte, the convenience of reaction product analysis and the electrochemical dehalogenation process of CH₃I on metal foils were also preliminarily reported³⁷. The polarization response curve of CH₃I reduction reaction (CH₃IRR) on EC-Cu has been first explored to examine the potential window of *in situ* methyl generation in our system (Figure 4.4a). Unlike the background curve representative of hydrogen evolution reaction (HER) under Ar atmosphere, the addition of CH₃I generates a distinctively strong electroreduction peak. The onset potential is

around -0.1 V vs reversible hydrogen electrode (RHE). It is worth noting that Cu does not behave as an inert electrode, but exhibits its catalytic behavior towards CH_3IRR . The onset potential of the same reaction on a glassy carbon electrode is more than 200 mV negative along with a much smaller cathodic peak, relative to that on Cu. The higher dissociation kinetics of CH_3I on the Cu surface may be attributed to the affinity between Cu and I^{38} . To further explore the influence of electrolysis induced surface pH variation, pH-dependent CH_3IRR was also conducted (Figure 4.4b). No noticeable peak shift was observed under the scale of standard hydrogen electrode (SHE) when the electrolyte was changed from 0.1 M KHCO_3 to $0.1\text{ M K}_2\text{CO}_3$ and 0.1 M KOH , indicating that any proton concentration effect on CH_3I dissociation if existing is negligible. Chronoamperometry experiments were then used to further study the potential dependency of CH_3IRR . The reduction products were collected and identified by gas chromatography (GC) and NMR spectroscopy. We found that CH_4 and C_2H_6 are the only two products generated from CH_3IRR (Figure 4.4c) while H_2 and CH_3OH are two by-products derived from HER and CH_3I hydrolysis, respectively. It was also found that the production ratio between C_2H_6 and CH_4 is potential dependent. Under -0.2 V vs RHE, a 67.7% faraday efficiency (FE) towards CH_4 and a 27.5% FE towards C_2H_6 was achieved. The C_2H_6 FE decreased down to 0% when -1 V vs RHE was applied, where HER became the dominant reaction. This observation suggests that the methyl generation and C-C coupling are likely to be mediated by the Cu surface while competing with the H_2 evolution. It is worth noting that CH_3I is not the only reagent that can be electrochemically reduced to the methyl group on the Cu surface. Generally, we believe that $^*\text{CH}_x$ can be generated by electrochemical dehalogenation reactions of various halomethanes and polyhalomethanes under similar conditions³⁹.

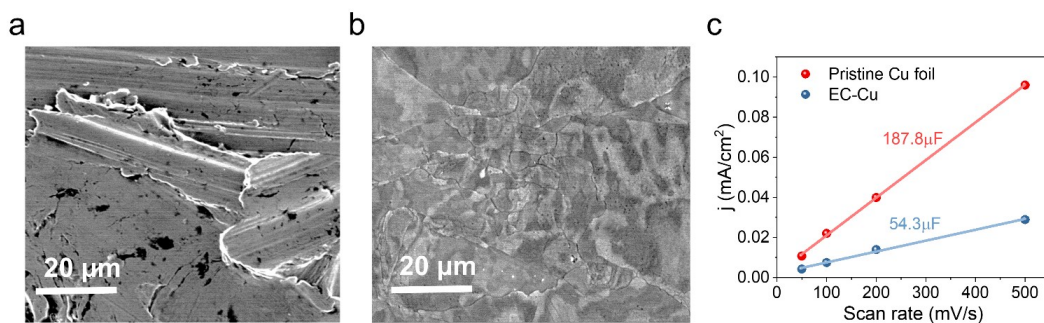


Figure 4.2. Structural characterization of Cu foil before and after electrochemical polish. SEM images of (a) pristine Cu foil and (b) Cu foil after electrochemical polish (EC-Cu). Double-layer capacitances of both pristine Cu foil and EC-Cu. Apparently, the surface flatness of Cu foil after electrochemical polish is significantly improved.

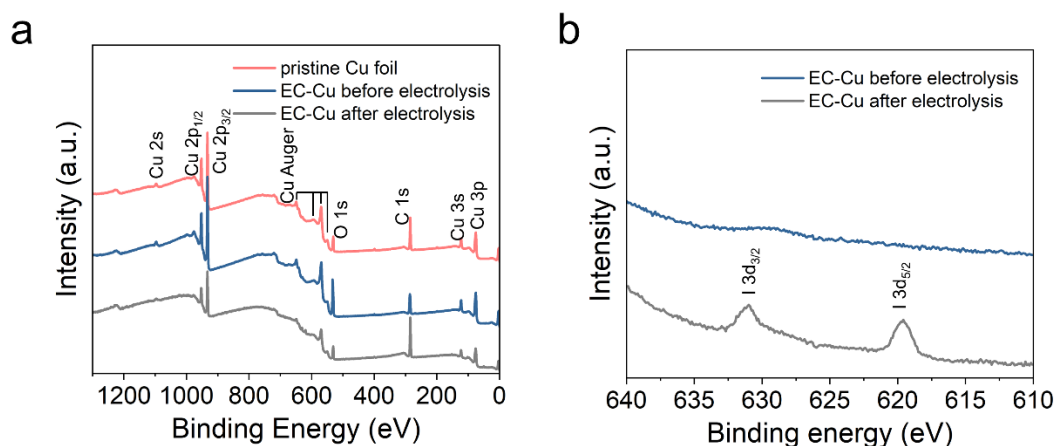


Figure 4.3. Elemental characterization of Cu surface through XPS. (a) XPS survey of pristine Cu foil, EC-Cu and the EC-Cu after CH_3I related electroreduction experiments. (b) The XPS spectra of I 3d before and after electrolysis.

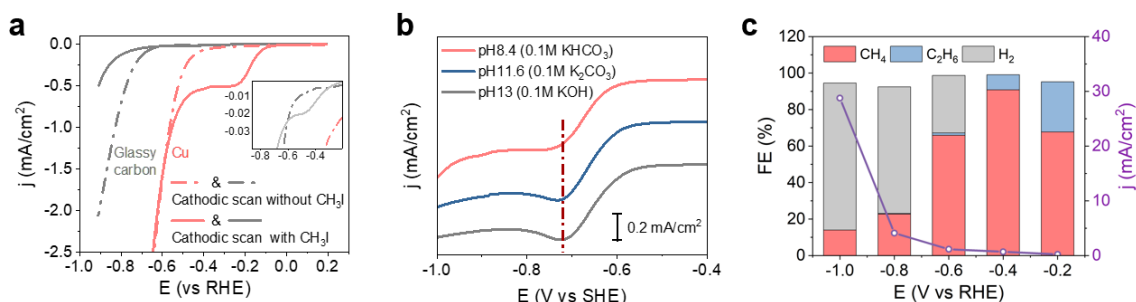


Figure 4.4. (a) The polarization response curve on the EC-Cu and glassy carbon electrodes with and without CH_3I . (b) The pH independence of characteristic CH_3I reduction peak position on EC-Cu against the SHE scale. (c) Potential dependent Faraday efficiency (FE) of different CH_3IRR products and their corresponding current densities during CH_3I electroreduction on EC-Cu.

4.3.2 CO chemical behavior on Cu under reductive potentials

CO was then introduced into the electrolysis system as another important building block in C-C asymmetric coupling on Cu surface. As a reference, the CO self-coupling ability on EC-Cu within the potential window from -0.2 to -1.0 V vs RHE was also shown (Figure 4.5a). Due to the low solubility and inert property of CO in 0.1 M KHCO_3 electrolyte¹⁰, multicarbons generated from CO reduction reaction (CORR) can only be detected under the potentials negative than -0.8V vs RHE and the total Faraday efficiency (FE) towards CORR is less than 10%. Despite being minor products, the liquid product

signals from CO self-coupling (Figure 4.5b) still can introduce uncertainty if they are not appropriately differentiated from the signals from CH₃-CO asymmetric coupling products.

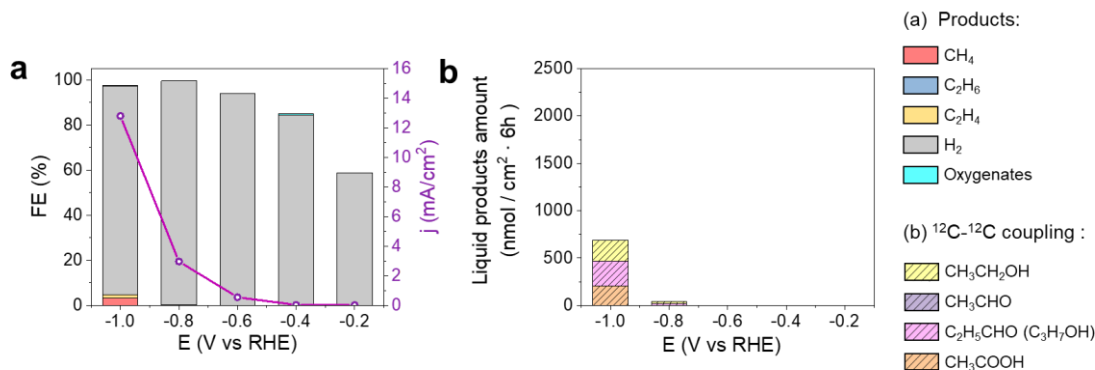
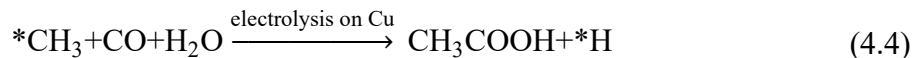
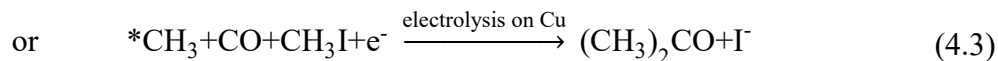
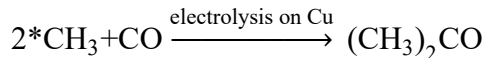
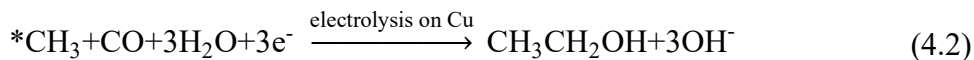
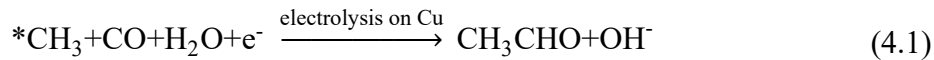


Figure 4.5. Potential dependent (a) product FEs and corresponding current density and (b) liquid products (multicarbon oxygenates) production amount and distribution of CO electroreduction on EC-Cu. The loss of FE under -0.2 V and -0.4 V vs RHE in the CORR is due to the low current densities on EC-Cu.

4.4 Validating the asymmetric coupling process over electrochemically polished Cu foil with isotope labeled co-reduction experiments

The introduction of a ¹³C isotope labeled reactant into the experiment is an effective method to remove this uncertainty. Specifically, the presence of a ¹³C atom will induce the characteristic coupling to the surrounding protons and makes them distinguishable in the ¹H NMR spectrum. The co-reduction experiments were executed with CO gas and liquid-phase ¹³CH₃I as the starting chemicals. No new gas product was observed from GC. With similar product species and potential dependency, the gas product spectrum appears to result from the combination of ¹³CH₃IRR and ¹²CORR (Figure 4.6a). Nevertheless, several sets of the new proton peaks previously absent in the CORR-only spectrum could be identified in the NMR spectrum, which was rigorously assigned to the four multicarbon oxygenates generated through ¹³CH₃-¹²CO asymmetric coupling (Figure 4.6b). Importantly, these asymmetric coupling products do not show up under the open circuit potential (OCP) while all other conditions are kept the same. This indicates that this co-reduction reaction is an electrocatalytic process and the corresponding equations are proposed as follow (equation 4.1 - 4.4):



The potential-dependent generation rates of isotope labeled multicarbon oxygenate were also quantified to further understand the asymmetric coupling process (Figure 4.6c). We found that the multicarbon oxygenate production rate resulting from asymmetric coupling first increases from 1525 nmol/(cm²·6h) to 8259 nmol/(cm²·6h) when the applied potential switch from -0.2 V to -0.8 V vs RHE, as the CH₃IRR partial current density increases, and the absorption of CO on Cu is also stronger⁴⁰⁻⁴¹. Further increasing the applied potential to -1.0 V vs RHE inhibits the asymmetric coupling. This can be attributed to the overwhelming HER and competitive CORR pathways. Acetaldehyde (CH₃CHO) is the major product in the co-reduction experiments under the wide potential range, generated by either the hydrogenation of *CH₃-*CO asymmetric coupling intermediate or the coupling between *CH₃ and *CHO. Based on the observation from CH₃IRR and CORR (Figure 4.4c and 4.5a), and the spectroscopical evidence in literatures^{13, 17}, the hydrogenation of CO requires a large overpotential. Therefore, the coupling between *CH₃ and *CO is more likely to be the first step. Ethanol (CH₃CH₂OH) was found to be another asymmetric coupling product existing from -0.6 V to -1.0 V vs RHE, which can come from the further electroreduction of CH₃CHO⁴². It is worth noting that although H₂O is illustrated as one of the proton sources in eq. 1 and eq. 2, the proton can be actually more broadly derived from bicarbonate and *H in HER. Acetic acid (CH₃COOH) and acetone ((CH₃)₂CO) were also found as two minor products from the isotope labeled co-reduction experiments. Instead of being hydrogenated, acetic acid and acetone are produced through further coupling processes between the *CH₃-*CO intermediate with H₂O or *CH₃/CH₃I. Although the generation rates of CH₃COOH and (CH₃)₂CO are influenced by the applied potential, they are not as potential-sensitive as CH₃CHO and CH₃CH₂OH.

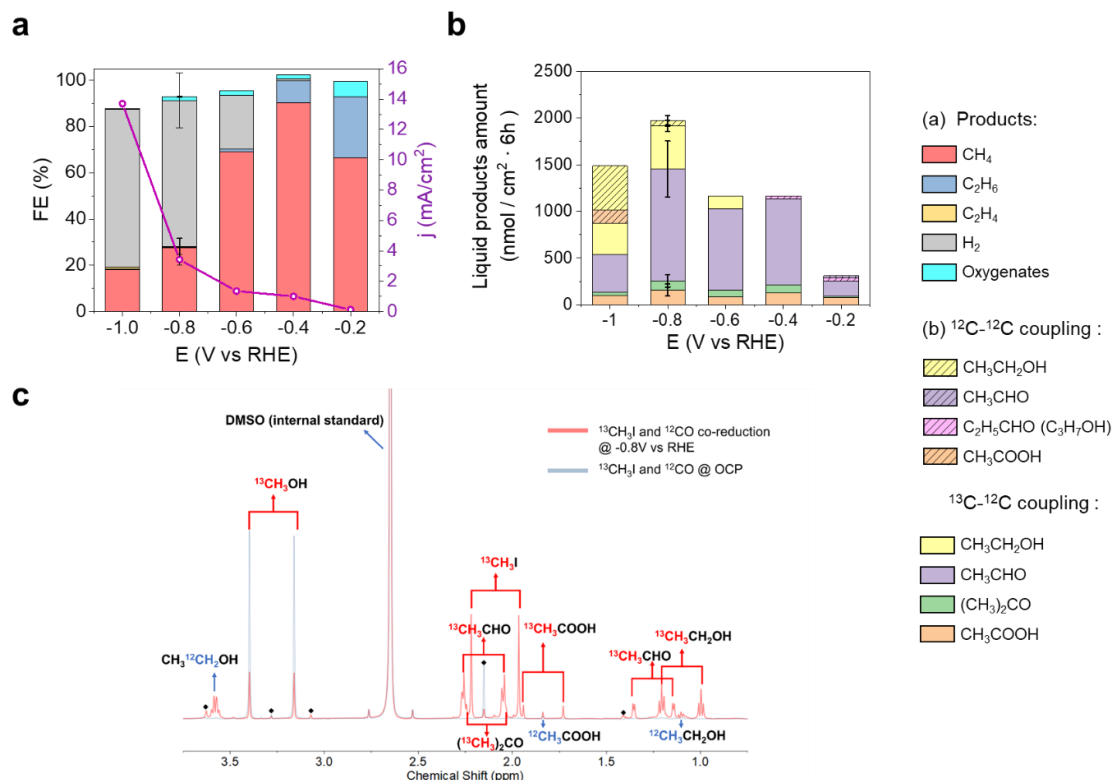


Figure 4.6. Potential dependent (a) product FEs and corresponding current density and (b) liquid products (multicarbon oxygenates) production amount and distribution of CO and CH_3I co-reduction on EC-Cu. Asymmetric products are quantified by isotope experiments. Error bars (1 SD) are based on the average value of three separate experiments results. (c) NMR spectra of liquid products from CH_3I and CO co-reduction experiments. Identified peaks are labeled with corresponding products. The blue color is used to highlight the products/protons that are related to C-12 while the red color is used for C-13. Unidentified minor peaks are labeled with diamond marks, which may come from trace impurities in the CH_3I reagent and CH_3I -induced leaching of the rubber sealing components. It is clear that no coupling reaction happens at the open circuit potential, which shows a flat baseline. $^{13}\text{CH}_3\text{OH}$ mainly comes from the hydrolysis of $^{13}\text{CH}_3\text{I}$, which is not the target product in this effort.

4.5 Exploration of asymmetric coupling mechanism boosted CO_2RR performance with Cu-Ag nanoparticle assembly tandem catalyst

The co-reduction experiments using two individual intermediates sources combined with isotope labeling provided us with concrete evidence on $^*\text{CH}_3$ - $^*\text{CO}$ asymmetric coupling on a model EC-Cu system. We then further extended the research objectives from model system-based mechanism exploration to practical CO_2 electrolysis with nanocatalysts to advance our understanding of asymmetric coupling. To this end, a Cu-Ag bimetallic

nanoparticle (NP) assembly was employed here as the catalytic platform to explore the asymmetric coupling in CO₂RR. The colloidal synthesis of both 7nm Cu and 7nm Ag NPs followed our group's previously developed methods³¹⁻³³. As an electrochemical tandem design principle, Ag can serve as a CO generator (equivalent to carbonyl branch in the W-L pathway) while Cu as a *CH_x generator²⁷⁻²⁸ (equivalent to methyl branch in the W-L pathway) for such asymmetric coupling. According to previous research, such Cu NPs on glassy carbon exhibit high selectivity towards methane⁴³ while Ag NPs were found to be a good CO-producing catalyst with nearly unity faradaic efficiency³². While the intermediates on the Cu are hard to be directly probed during electrolysis, CO and CH₄ generation rates can be easily measured and serve as an alternative way to indirectly monitor the corresponding surface chemistry. Therefore, we chose a potential range where Ag NPs selectively produce CO while Cu NPs generate CH₄ as the main product.

The prepared monodisperse 7nm Cu NPs (Figure 4.7a) and Ag NPs (Figure 4.7b) were spin-coated onto a glassy carbon to form a dense monolayer, which was then used for CO₂RR (Figure 4.7c). Post-electrolysis characterization of Cu-Ag nanoparticles was also conducted to explore any other possible factors besides the tandem effect that may influence the catalytic performance. Scanning electron microscopy (SEM) imaging, scanning transmission electron microscopy (STEM) imaging, together with energy dispersive and electron energy loss spectroscopy (EDX and EELS) elemental mapping, show that Cu NPs migrated and agglomerated together to form a network during the CO₂ electrolysis due to the dynamic nature of Cu nanoparticles (Figure 4.8 and 4.9). Ag particles were found to grow larger but remain isolated on such a Cu-Ag network. The nanodomains and the interfaces between Ag and Cu were further characterized by HR-TEM (Figure 4.10). These results suggest that the Cu and Ag domains are in close contact with each other during CO₂RR rather than spatially separated on the as-prepared glassy carbon electrode. The XPS spectra of Cu and Ag indicate that no appreciable electronic interaction between Cu and Ag exists (Figure 4.11)⁴⁴.

Although *CH₃ generation in the co-reduction experiments can happen at potentials as positive as -0.1 V vs RHE due to external feeding of CH₃I reagent, the hydrodeoxygenation of *CO intermediates to *CH_x intermediates on Cu during CO₂RR usually happens under relatively negative potentials. Pure Cu NP assembly, which is denoted as Cu100, was found to produce a significant amount of CH₄ within the potential window from -1.05 to -1.35 V vs RHE (Figure 4.7d). A maximum CH₄ production rate of 4.66 nmol/s was achieved at -1.2 V vs RHE. When a more negative potential was applied, the overwhelming HER suppresses the CO₂ chemistry on Cu. Taking advantage of the tandem strategy, a certain fraction of the Cu NPs was replaced with Ag NPs to tune the catalytic CO₂ transformation rates towards both CO and CH₄. By increasing the Ag NP ratio from 0% to 50%, CO generation rate at -1.2 V vs RHE was enhanced from 0.22 nmol/s to 2.95 nmol/s. Meanwhile, since CO is a key intermediate in the production of CH₄ and functions as a competing adsorbate that suppresses HER, the generation of CH₄ on Cu sites may also benefit from the addition of Ag, especially under relatively negative potentials. An aligned production rate of CO and CH₄ was achieved with Cu50Ag50 at -1.2 V vs RHE. Under such conditions, a 0.73 nmol/s production rate towards multicarbon oxygenates was observed on Cu50Ag50, which is 9.6 times higher than that on Cu100.

To corroborate the early observation in the isotope co-reduction experiments, the correlation between multicarbon oxygenate production rates in tandem CO₂RR and the production rates of CO and CH₄ were also analyzed (Figure 4.7e). While the asymmetric coupling needs both *CO and *CH_x intermediates on the Cu surface, we defined the lower value between CO and CH₄ production rate under a particular reaction condition as a rate-determining dimensionless indicator to describe the co-existence of CH₄ and CO. Taking CO₂RR on Cu₅₀Ag₅₀ as an example, the production rate of CO and CH₄ under -1.2 V vs RHE are 2.75 and 2.95 nmol/s respectively. Therefore, the value representing the co-existence of CH₄ and CO is then defined as 2.75. It was found that the production rates of oxygenates obey well the same trend as the co-existence of CH₄ and CO value change. Even though the apparent production rates alone are not sufficient to further discuss the causality, a strong correlation between the two can be confirmed. Since a similar phenomenon and trend can be observed in both the electrochemical tandem CO₂RR and the isotope co-reduction experiments, our study suggests possible asymmetric coupling pathways for multicarbon products, which leads to a catalytic selectivity shift towards oxygenates. From this study, we envision that various tandem systems can be developed for more efficient and selective electrocatalytic CO₂RR benefiting from W-L pathway inspired asymmetric coupling.

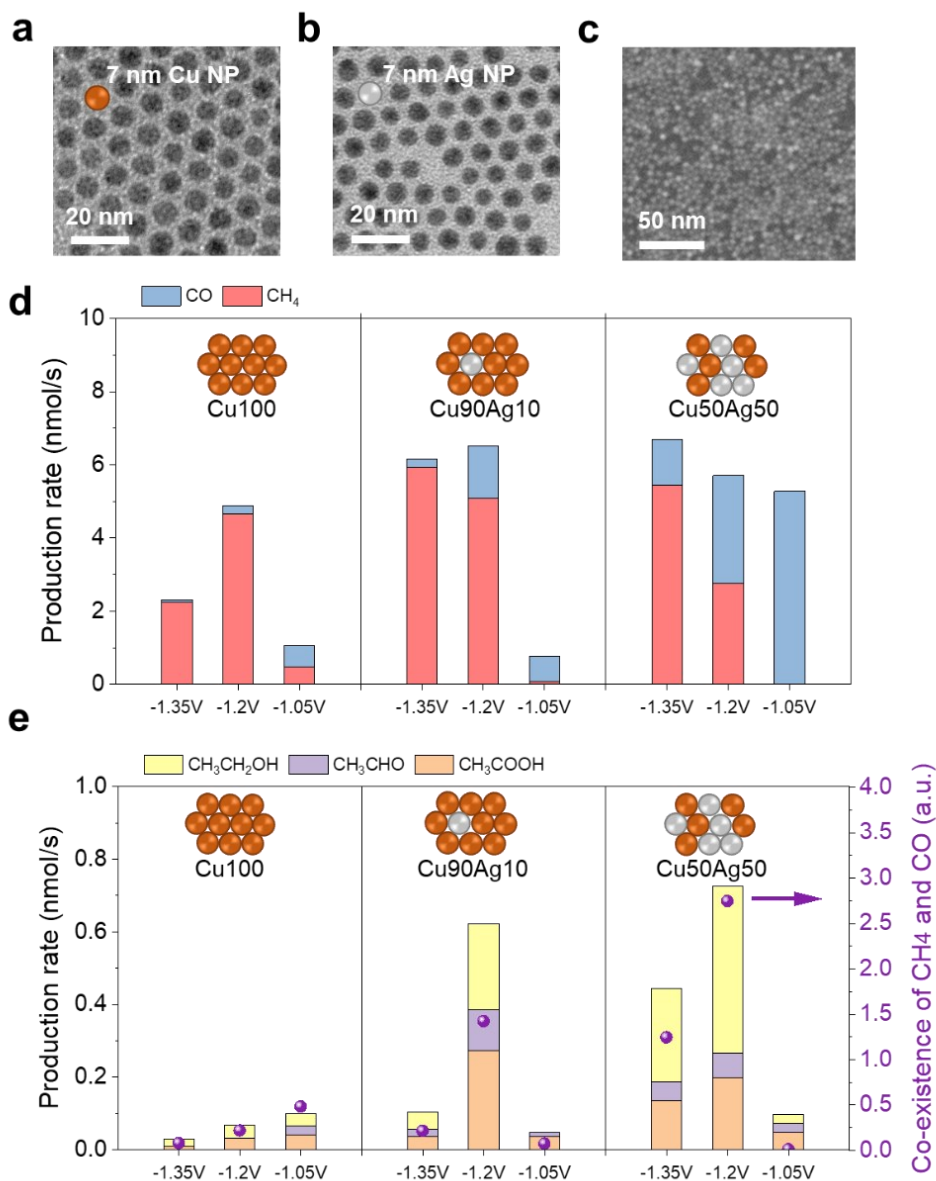


Figure 4.7. TEM images of (a) 7nm Cu nanoparticles and (b) 7nm Ag nanoparticles. (c) SEM image of as-prepared Cu-Ag nanoparticles assembly on glassy carbon as the working electrode. (d) Potential dependent production rates of CO and CH₄ as two intermediates indicators in CO₂ reduction on Cu-Ag nanoparticles assembly electrodes with varied Cu-Ag ratios. (e) Potential dependent multicarbon oxygenate production rates in CO₂ reduction on Cu-Ag nanoparticles assembly electrodes with varied Cu-Ag ratios. The co-existence of CH₄ and CO is a dimensionless indicator defined as the minimum value between CO and CH₄ production rates, which indicates the limiting factor for asymmetric coupling. All potentials here are described under the RHE scale.

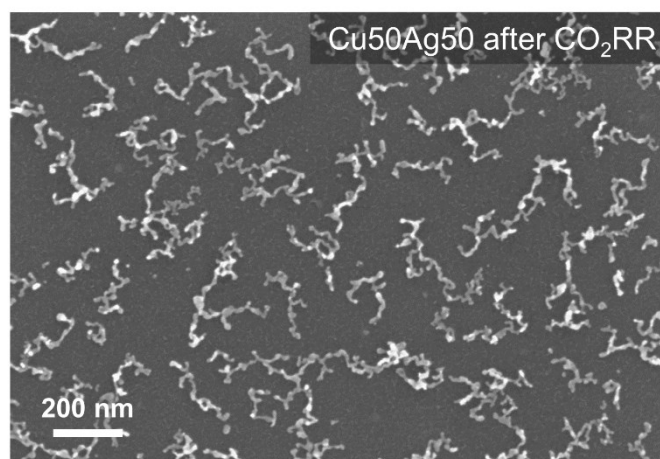


Figure 4.8. SEM image of Cu50Ag50 after CO₂ electrolysis. Based on the SEM image, nanoparticles evolved into dendrite structures.

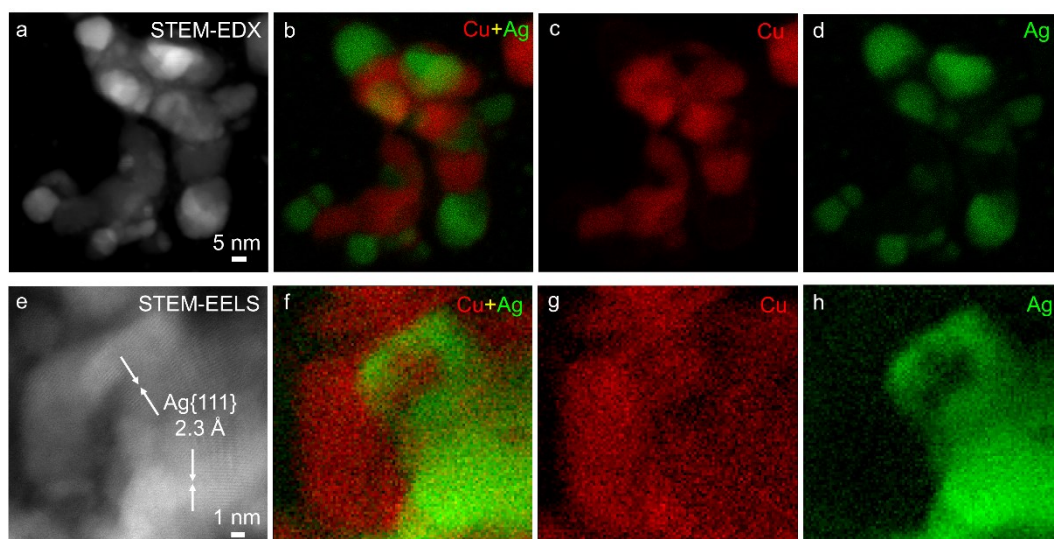


Figure 4.9. Elemental analysis of the dendrite-like nanoparticles formed during CO₂RR. (a-d) HAADF-STEM image (a) and corresponding EDX composite map of Cu (red) and Ag (green) (b), Cu map (c), and Ag map (d), based on the Cu K and Ag L edges. (e-h) Atomic-scale STEM image with Ag {111} d-spacings labeled by arrows (e) and EELS composite maps of Cu and Ag (f), Cu map (g), and Ag map (h), based on Cu L and Ag M edges. Both STEM-EDX and STEM-EELS elemental maps show that Ag nanodomains are embedded in the Cu network in close proximity, which also indicates the significantly higher mobility of Cu during the CO₂RR, relative to isolated Ag domains.

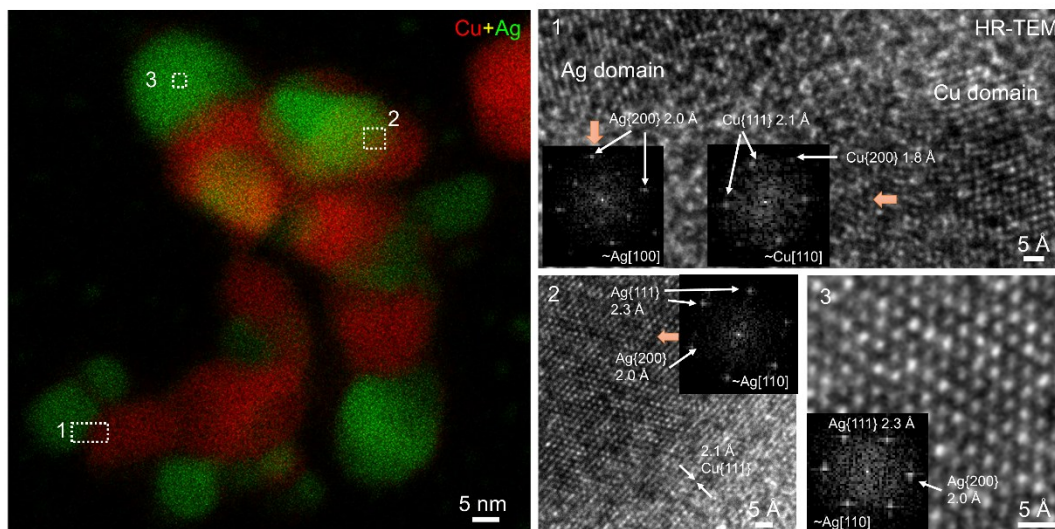


Figure 4.10. HR-TEM images of the representative Ag and Cu nanodomains, corresponding to certain regions in the STEM-EDX elemental maps. Regions 1 and 2 show the interface of Ag and Cu nanodomains, while Region 3 shows a predominant Ag single-crystal domain on the [110] zone axis.

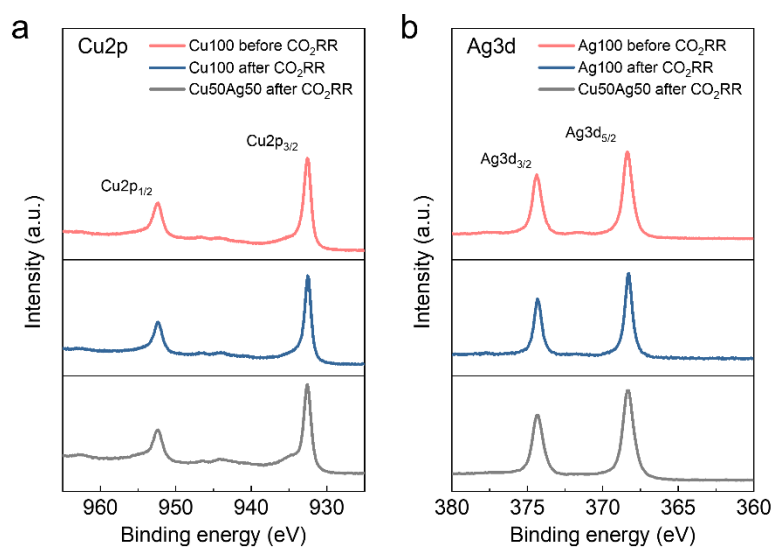


Figure 4.11. XPS spectra of Cu and Ag nanoparticles before and after CO₂ electrolysis. No peak shifting can be found in both (a) Cu and (b) Ag spectra, which indicates the product spectrum difference in different nanoparticle assemblies is not due to the strong electronic interaction between Cu and Ag.

4.6 Conclusion

In summary, we explored the bio-inspired asymmetric C-C coupling in CO₂RR by both the isotope labeled co-reduction experiments and Cu-Ag electrochemical tandem catalysis in practical CO₂ electroreduction conditions. We first validated the characteristic catalysis process of *CH₃-*CO asymmetric coupling on the Cu surface. Since the C-C coupling intermediate species are challenging to be directly probed, we developed an isotope labeled co-reduction process to explore the *CH₃-*CO coupling on Cu. Within a wide potential window, asymmetric *CH₃-*CO coupling can happen on Cu and yield up to four detectable isotope labeled oxygenate products including acetaldehyde, ethanol, acetic acid, and acetone. Hydrogenation is necessary for the production of acetaldehyde and ethanol from the asymmetric coupling intermediate, while acetic acid and acetone are generated through an additional coupling process. After confirming the Cu catalyzed asymmetric C-C coupling in the model system, Cu-Ag nanoparticle assembly was used as a tandem catalyst for CO₂ electroreduction in order to further explore the asymmetric coupling in more practical conditions. The production rate of *CH_x and *CO intermediates during CO₂RR can be successfully tuned by tuning the mass ratio between Cu and Ag in the tandem system. The final oxygenates generation rates are found strongly correlated with the co-existence of both intermediates. Maximized oxygenate generation rate can be achieved when these two intermediates are generally aligned. These new insights of the C-C coupling pathway in CO₂ fixation not only confirmed the existence of asymmetric coupling, as a supplementary to well explored *CO-*CO symmetric coupling pathway but also shed light on the new design paradigm of tandem catalytic systems in future CO₂ electrolysis.

4.7 References

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Chapter 5 Summary and Outlook of the CO₂RR

In this chapter, I would like to first summarize my efforts and conclusions of the whole dissertation and then more broadly talk about my personal outlook on the CO₂ electrocatalysis future.

In the first chapter of the dissertation, I focus on introducing the background, motivation, challenges, and progress in the field of CO₂ electroreduction. I hope that through this introduction, readers can get a big picture of the CO₂RR area and its current status. Meanwhile, the introduction of catalytic strategies, especially the tandem strategy in this chapter, also clarifies the major research directions of the subsequent chapters of this dissertation.

Chapter 2 is my first effort at tandem catalytic strategies in my graduate research. As a preliminary exploration of the tandem strategy, we are committed to studying the feasibility and universality of the tandem strategy. Therefore, a gas diffusion electrode that is closer to the industrial application was selected to study the tandem strategy under large operating current density. By tuning the ratio of Cu-Ag bimetallic catalysts, the tandem strategy has been proved to significantly improve the production rate of multicarbon products in CO₂ reduction. We also verified that there is no strong mutual interaction between Cu and Ag in this system. Additionally, by analyzing the results, we found that the intrinsic activity of the Cu in the tandem system is higher than its performance under pure CO₂, or even CO atmosphere. These observations raise two interesting questions, which correspond to my research in the next two chapters, respectively. First, can Cu and Ag form stable alloys under electrochemical conditions? Or more generally, what is the thermodynamic steady state of Cu and Ag under electrochemical conditions? Second, how can the special intrinsic activity of the Cu in the tandem system be correlated to the molecular transformation mechanism?

Chapter 3 focuses on the structural evolution of Cu-Ag bimetallic catalysts during CO₂ electrolysis. Through detailed time-dependent *ex situ* electron microscopy characterizations, we realize that Cu tends to gradually leach out from the nano-alloy to form individual grains during electrocatalysis. Meanwhile, the content of dopant atoms in the Cu-rich and Ag-rich phases also decreases to a thermodynamically stable value. Pb-UPD and *operando* HERFD XANES and EXAFS techniques were also utilized to perform more *in situ* characterizations of the nano-alloy surface structure, further complementing our understanding of the structural evolution of Cu-Ag nano-alloy under

CO₂RR. However, due to the complexity of surface characterization of nanomaterials, it is difficult to probe the specific distribution of surface atoms in current efforts. In addition, whether electrochemistry can offer sufficient driving force to make the mechanically mixed pure Cu and pure Ag nanoparticles also evolve into a thermodynamically stable alloy phase requires further investigation.

Chapter 4 mainly explores the C-C coupling pathway existing in the tandem system. Inspired by the Wood–Ljungdahl pathway, we conjecture that in the tandem system, in addition to the common CO-CO coupling, there is also an asymmetric CH_x-CO coupling pathway, which facilitates the generation of multicarbons. Therefore, we first designed ¹³CH₃I and ¹²CO isotope co-reduction experiment, in which Cu was confirmed to be able to catalyze the asymmetric CH_x-CO coupling. We then constructed a monodisperse Cu and Ag nanoparticle assembly tandem system and observed a significant correlation between multicarbon oxygenate generation with asymmetric coupling intermediates in more practical electrocatalytic CO₂ reduction. We believe that the existence of alternative C-C coupling pathways is an important advantage of the tandem system to achieve a high production rate of multicarbon products, and also provides necessary theoretical support for the further development of tandem catalysis research.

There are still a lot of questions worth digging into for the tandem CO₂RR. For example, how to control the structure, proportion, and spatial distribution of the Cu and the Ag on the electrode to further improve the CO₂RR catalytic performance. More broadly, instead of designing the tandem system based on CO, can other C1 products or intermediates be utilized to enrich the tandem catalytic strategies? Meanwhile, there is still a long way to go for the adaptability and optimization of the tandem system in the membrane electrolyzer.

When our vision is not limited to the application of the tandem strategy in CO₂ electroreduction, but to discuss the future development prospects of CO₂ utilization in a more general way, we should realize that CO₂ reduction is still at the beginning stage, just like the development of water splitting and fuel cells. As a scientific field of great interest, the CO₂ electroreduction community has contributed a lot to the development of advanced catalytic strategies, electrochemical three-phase interfaces, more accurate first-principles modeling and computational methods, and the development of *in situ* characterization techniques. These contributions are not limited to CO₂ research but play an important role in supporting and promoting research in the broader field of chemistry. However, when we turn our attention to industrial CO₂ electroreduction, we will find that there are still many problems without satisfactory solutions, such as low energy efficiency and mass efficiency, carbonate salts deposition on the cathode, and catalyst stability problems. In addition, the source of CO₂ is also an issue that needs to be

carefully considered. Currently, the CO₂ collected by direct air capture (DAC) technologies is too costly to have any practical value for use. On the other hand, the low concentration of CO₂ in the flue gas and the existence of O₂, NO_x, and SO_x, put forward higher requirements for the electrolyzer and catalyst stability. Therefore, in order to make great progress in the electrochemical CO₂RR, the joint efforts between the CO₂RR community with the porous material community, polymer community, *etc.*, as well as close cooperation with the industry, are eagerly needed. Recently, some people feel like the pursuit of catalytic performance is hype, which is potentially encouraged by some academic journals. As time goes by, this upsurge will eventually subside, and the perspective of academic research will return to scientific issues centered on basic physical chemistry questions. Undeniably, this argument has practical significance, but it is worth pointing out that using a reductionist perspective to view the development of a field is also biased. Respecting the purity of scientific research and the complexity of field development are two sides of reality. Agreeing with the unity of opposites of contradictions, and fully conducting cross-industry and cross-regional communication and cooperation is the key to truly promoting the development and the application of CO₂ electroreduction technology in the next few decades.